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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

82

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CONDUCTED BY

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THE

CHEMICAL GAZETTE.

No. XXIX.—January 1, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Iodides. *By* M. LABOURÉ.

THE soluble iodides are able to dissolve iodine in variable proportions according to the degree of concentration of the solution of the iodide; the quantity of iodine dissolved is in direct ratio to the state of concentration. M. Baup, and some other chemists, consider the ioduretted iodides as definite compounds. This view I am not disposed to admit, all facts being opposed to it.

1st. These products are uncrystallizable, and colour immediately the filters and organic substances just in the same manner as free iodine.

2nd. Placed in contact with a solution of starch, there is immediate production of a blue colour.

3rd. Treated with æther, the iodine dissolves, while the iodide remains in solution in the water, and forms a transparent and colourless layer in the lower portion of the tube.

4th. When a current of sulphuretted hydrogen is passed into the solution, hydriodic acid is formed and a deposit of sulphur, and the solution becomes colourless. A solution of an alkaline iodide saturated with iodine may be employed with great advantage in preparing hydriodic acid; it may be obtained in a nearly fuming state, but it is necessary to have recourse to distillation, which always gives a coloured acid.

5th. The ioduretted iodides placed in contact with iron filings lose their colour as the iron combines with the iodine; at the same time there is an elevation of temperature. From these characters, which are those of free iodine, I consider the ioduretted iodides as simple solutions of iodine in the iodide, and not as compounds. I have observed, conjointly with M. Cloez, that on treating the iodide of potassium with concentrated sulphuric acid, there is always a disengagement of sulphuretted hydrogen, which can only take place with the decomposition of the sulphuric acid. This acid acts with great

energy and production of heat; violet vapours of iodine are formed, which become brown, and condense in the higher portion of the tube into a liquid of the same colour. Among the gases which we particularly noticed were sulphurous and hydrosulphuric acids; there is moreover a separation of iodine, which settles at the bottom of the tube. This decomposition is very complex and difficult to explain, both on account of the number of products which originate, as from the difficulty of separating them. Hitherto, in the preparation of iodine from the mother-waters of the Varech sodas, the disengagement of sulphuretted hydrogen had been exclusively attributed to the accidental presence of sulphurets in the mother-waters. According to M. Cloez, the oxygen of the sulphuric acid combines with the iodine to form iodic acid; but, notwithstanding all my efforts, I have not been able to detect its presence, so that I am still ignorant as to what becomes of the oxygen. I hope soon, however, to be able to take up the subject again, and to obtain more satisfactory results.

I have since observed that the iodide of potassium is not the only one which liberates sulphuretted hydrogen, but that the majority of the soluble iodides likewise give off some of this gas when treated with sulphuric acid; while the greater portion of the insoluble iodides are attacked more or less easily, with or without the assistance of heat, by this acid, and for the greater part only afford sulphurous acid gas, a sulphate, and iodine, without the least trace of sulphuretted hydrogen.

According to M. Thénard, hydrochloric acid has no action on the iodides; it decomposes, however, a large number, and affords very different products. According to Serullas, liquid hydrochloric acid decomposes the iodide of nitrogen, the iodine being converted into iodic and hydriodic acids, by combining with the oxygen and a portion of the hydrogen of the decomposed water, while the other portion of the hydrogen unites with the nitrogen to form ammonia, which enters into combination with the hydrochloric acid. Nearly at the same time the excess of hydrochloric acid determines a reaction among its own elements and those of the iodic and hydriodic acids, so that there is formed water and the subchloride of iodine, which remains in solution. This second reaction does not however take place altogether in this manner, for the hydrochloric acid has no action on the hydriodic acid; and this latter not requiring the presence of the hydrochloric acid to decompose the iodic acid, it results that the hydrochloric and hydriodic acids act at the same time on the iodic acid and decompose it, giving rise to water, while the chlorine of the hydrochloric acid enters into combination with the iodine from the iodic and hydriodic acids to form protochloride of iodine.

The solid alkaline iodides, those of potassium, barium, sodium, ammonium, and some others, placed in contact with concentrated hydrochloric acid, colour it even in the cold; but when heated to boiling, it becomes of a more or less deep yellow; and if, after cooling, the acid be decanted, and the residue washed several times

with alcohol of 0·828 spec. grav., in order to remove the whole of the acid and of the alkaline iodide, a pulverulent residue is obtained, which consists solely of alkaline chloride, which dissolves entirely in water, and affords with nitrate of silver a white curdy precipitate which is soluble in ammonia.

The iodide of zinc dissolves in cold hydrochloric acid, and colours it yellow.

Hydrochloric acid has no perceptible action in the cold on the yellow iodide of lead, but when boiled the iodide dissolves entirely if there be sufficient acid; the solution is transparent, slightly reddish-yellow; on cooling, some pale yellow acicular crystals separate, which are sometimes arranged in rays, and consist of small four-sided prisms. After having decanted the acid, they are washed quickly once or twice with distilled water, as they are decomposed by being kept long in contact with water. These crystals are composed of chloride and of iodide of lead (chloro-plombate of protiodide of lead).

The iodides of antimony and of bismuth dissolve in boiling hydrochloric acid, and impart to it a red colour.

According to M. Rammelsberg, the iodide of lead does not combine with ammonia in the moist way, but only in the dry way, and forms a white mass composed of PbI, NH^3; this product may however be obtained in the moist way; on placing either amorphous or crystallized iodide of lead in water in contact with caustic ammonia, it becomes white, and after several days of contact a white paste is obtained, which is not changed by exposure to the air in drying, and which is the iodo-plombate of ammonia; on being heated it disengages the ammonia.

M. Rammelsberg also states that the protiodide of copper dissolves readily, although in small quantity, in solution of ammonia, without colouring it, but that no compound is obtained in the moist way. I have however obtained this compound with a salt of the protoxide of copper, prepared by M. Levol's method, by saturating with ammonia the solution of a salt of binoxide of copper, then immersing some slips of copper in the liquid, filling the flask with boiling distilled water, closing it air-tight, and shaking it now and then until decoloration ensues. Some solution of iodide of potassium is then placed in a test tube, and the protosalt of copper poured on to it; the test-tube is immediately closed, when there is formed a white crystalline precipitate, and at the same time some brilliant white prismatic crystals are deposited on the sides of the tube. These crystals, as well as the precipitate, consist of protiodide of copper and of ammonia (iodo-cuprite of ammonia). They cannot be dried without decomposition; as soon as they have been removed from the liquid they disengage ammonia, and become of a green colour; the liquid in which the crystals were deposited remains colourless for some instants, but it gradually becomes blue, and is converted into a compound of biniodide of copper and of ammonia (iodo-cuprate of ammonia).

The protochloride of tin decomposes the iodides of mercury. The

protiodide in contact with its solution becomes gradually greenish-black, then entirely black, and subsequently the mixture is of a grayish slate colour, from the precipitated intermixture of oxide of tin. The biniodide of mercury becomes yellowish-red under the same circumstances, then yellow, greenish-yellow, and at last wholly green, being gradually reduced to the state of protiodide. If there is an excess of chloride of tin, it is decomposed as above; finely-divided metallic mercury and oxide of tin are precipitated, and the liquor contains hydriodic and hydrochloric acids, which hold some of the tin in solution.

The alkaline and other soluble iodides, those of ammonium, magnesium, of iron, of zinc, &c., decompose the protochloride of mercury. This fact appears somewhat extraordinary, when it is considered how little stable is the protiodide of this metal.

The solid iodides, and those dissolved in distilled water, likewise affect the decomposition; on being brought into contact the calomel assumes a greenish-gray tint; when the mixture is triturated in a mortar, it becomes of a deep green; placed in darkness, it will remain for a considerable length of time green, notwithstanding the presence of an excess of alkaline iodide, while if exposed to the light the decomposition is effected much more rapidly; the mixture passes from green to yellow, then to red; at the same time some globules of metallic mercury are observed. In these various reactions the calomel is converted into protiodide of mercury and alkaline chloride, which is easily demonstrated by treating the green mixture twice or thrice with alcohol of 0·828 spec. grav., which removes the whole of the excess of alkaline iodide; the residue is then treated with distilled water, which dissolves the alkaline chloride, which may be obtained in crystals, and is easily recognised by the nitrate of silver, which gives a white curdy precipitate of chloride, characterized by its solubility in ammonia. After these two operations, the residue is dried; it is a mixture of protiodide of mercury and calomel; it is then heated in a tube closed at one end; the protiodide of mercury, which is partly decomposed, disengages vapours of metallic mercury, which condense in small globules, and form a ring of whitish gray; immediately beneath it is deposited a second greenish-yellow ring of sesqui-iodide of mercury; and lastly, the calomel being less volatile, sublimes at the end of the operation, and forms a white ring beneath the preceding one.

With respect to the change of colour of the green mixture after exposure to the light for some days, this is owing to the secondary action exerted by the alkaline iodide on the protiodide of mercury. The protochloride of mercury may be entirely decomposed by an excess of alkaline iodide, as is seen on heating an intimate mixture of calomel and of alkaline iodide in excess; the mixture passes from green to yellow, then into red, fuses, and becomes of a blackish-brown; metallic mercury and some biniodide of mercury sublime, consequent upon the decomposition which the protiodide undergoes in the presence of alkaline iodides. If, when nothing further is disengaged, the tube be cut near the base with a file, the residue which

it contains will be found to be white, entirely soluble in water, and composed of alkaline chloride mixed with the excess of alkaline iodide.

Most of the double iodides are decomposed by water; the electro-positive iodide dissolves, while the electro-negative iodide is precipitated in an insoluble state. This was observed with the double iodides of protiodide of tin, iodide of lead, biniodide of mercury, iodide of silver, &c.

According to M. Boulay, when the biniodhydrargyrate of the iodide of potassium is treated with water, 1 atom of biniodide of mercury separates, and there remains some protiodhydrargyrate of iodide of potassium; but this compound does not actually exist, for it suffices to separate the biniodide which is deposited and to concentrate the liquid, in order to obtain acicular crystals of biniodhydrargyrate of iodide of potassium, which are intermixed with small cubes of alkaline iodide. Among the double iodides, the biniodhydrargyrate of iodide of potassium has the property of dissolving while boiling 1 atom of biniodide of mercury, which it deposits entirely on cooling in a crystalline state. M. Boulay likewise considered this iodide while in a boiling state as a triniodhydrargyrate of iodide of potassium, which is decomposed by cooling; but this compound does not exist any more than the preceding one.

The other compounds of biniodide of mercury with the alkaline iodides, and those of ammonium, of magnesium, iron and zinc, behave like the biniodhydrargyrate of the iodide of potassium.—*Journ. de Pharm.* for November.

On Iodine in the Urine. *By* J. W. Griffith, M.D.*

In my 'Manual of the Normal and Abnormal Characters of the Urine and its Deposits,' I have stated that iodine, when taken internally, generally, if not always, appears in the urine as an iodate, inasmuch as on boiling alcohol on the residue of evaporation the iodine is not removed.

From the examination of a large number of urines I have lately made, I have arrived at a somewhat different conclusion, viz. that the iodine does not pass into the urine as an iodate. Such opinion is founded upon the following experiments, which I have several times repeated:—

1st. The urine of a patient, taking the iodide of potassium, was allowed to cool; a few drops of aqueous solution of starch were then added; no iodide of starch was formed; thus showing that the iodine was not contained in the solution in a free state.

2nd. The same urine, after the addition of starch, produced a precipitation of the iodide of starch, when a few drops of nitro-muriatic acid were added; thus showing that the iodine exists in combination with some base, as a salt, requiring the exercise of the influence of an acid or acidifiable body, having greater affinity for the base than the iodine, or in other words, being capable of decomposing the iodic compound. What is this compound? Is it an iodide or

* Communicated by the author.

an iodate? To determine this, I proceeded thus:—Some of the same urine, giving a copious purplish-blue precipitate with starch after the addition of nitro-muriatic acid, was evaporated *completely* to dryness. Alcohol, which had been distilled off carbonate of potash, was then added and digested for some hours; more was added, and the residue was washed until little of the iodic compound came away with the spirit. To this spirituous solution, which was filtered, cold solution of starch and a few drops of nitro-muriatic acid were added, a copious purplish-blue precipitate of iodide of starch was formed; thus showing that the iodine existed in combination with some base, but not as an iodate, because the iodate of potassa is not soluble in alcohol. In my work I have stated that the iodine may be readily detected by the addition of a few drops of nitro-muriatic acid or solution of chlorine, and then the addition of a few drops of cold solution of starch. This fact is, as I shall show, inconsistent with the existence of the iodine in the urine as an iodate. A portion of pure iodic acid was dissolved in *Liquor potassæ* and distilled water. Upon the addition of starch and nitro-muriatic acid to this, no iodide of starch was formed. Upon digesting a little morphia in the mixture, without the addition of the *aqua regia*, the blue iodide appears as it does when sulphurous acid is passed through the same solution. The influence of some deoxidizing agent is requisite to decompose the iodic acid. When sulphurous acid is passed through urine containing the iodine mixed with a few drops of solution of starch, no iodide of starch is formed; thus showing that no iodate or iodic acid is present (the sulphurous acid does not elicit iodine from the iodide of potassium). The conclusions then that we must arrive at are—

1st. That there is no free iodine in the urine when an iodide has been taken internally.

2nd. That the iodine does not exist as iodate of potash, because sulphurous acid and morphia, which elicit free iodine from iodates, do not form this compound. Moreover, the iodic compound is soluble in alcohol, which an iodate is not.

3rd. That it exists in the form of an iodide, and is removable from the urinary residue both by alcohol and water.

Researches on Cerium. By M. Hermann.

To prepare a chemically-pure oxide of cerium, finely-pulverized cerite is dissolved in boiling muriatic acid, and the silica separated in the usual manner. The solution is neutralized with ammonia, and the peroxide of iron thrown down with succinate of ammonia. An excess of ammonia is then added to the filtered liquid, which causes a very voluminous precipitate, consisting of protoxide of cerium and oxide of lanthanium, contaminated by lime, magnesia, alumina and oxide of manganese. The precipitate is dissolved in nitric acid, evaporated to dryness, and the salt ignited; it is then reduced to a very fine powder, and digested with a very dilute nitric acid (2 parts of concentrated acid to 100 parts of water). The acid

dissolves the greater portion of the oxide of lanthanium and of the other bases, but leaves undissolved most of the oxide of cerium, which is mixed with traces of the oxides of lanthanium and manganese. This impure oxide of cerium is dissolved in sulphuric acid which has been diluted with equal portions of water; the solution is then mixed with 50 parts of distilled water, and the liquid made to boil. In this operation the liquid becomes opake, and deposits a sulphur-yellow precipitate, which is perfectly pure basic sulphate of cerium. All the oxide of lanthanium, which was mixed with the oxide of cerium, remains in the solution, which also contains a large quantity of the latter element. To obtain the last portions, caustic soda is added to the acid liquid, and the precipitate dissolved in nitric acid, the salt ignited, the free oxide of lanthanium extracted with dilute nitric acid, the oxide of cerium dissolved in sulphuric acid, the solution diluted and again boiled. A precipitate of basic sulphate of cerium is produced as before, which is as pure as the former.

If the oxides which are still contained in the acid liquid, boiled for the second time, be now examined, it will be found that they consist mostly of oxide of lanthanium mixed with much oxide of manganese and some little oxide of cerium.

Atomic Weight of Cerium.—23·523 parts of anhydrous sulphate of cerium gave 29·160 parts ignited sulphate of barytes. From this the atomic weight of the protoxide of cerium is calculated at 675·0, and with the supposition that the protoxide contains 1 atom oxygen, that of cerium will be 575·0, which nearly agrees with Rammelsberg's determination.

Protoxide of Cerium.—When caustic soda in excess is added to a solution of the protosulphate of cerium, a precipitate of the hydrate of the protoxide of cerium is formed, which appears, avoiding the access of air, colourless, transparent, mucous, and very similar to the hydrate of alumina. By exposure to the air it is converted into the hydrate of the peroxide of cerium, when it assumes a light brownish colour. When the hydrate is left for any length of time exposed to the atmosphere, the precipitate acquires a yellow colour, especially when an excess of alkali is present. This colour is not peculiar to the hydrate of the peroxide of cerium, but to the carbonate. Pure hydrate of the peroxide of cerium has a perfectly light brownish colour, which becomes darker on drying the preparation.

When operating with impure salts of the peroxide of cerium, it frequently happens that precipitates are thrown down from their solutions by alkalies, which rapidly assume a dark brown colour by exposure to the air. This colouring of the oxide of cerium does not however arise from didymium, but from manganese. The oxide of manganese constantly accompanies cerium and lanthanium, and it is hidden in such a manner in its combination with the oxides of these metals, that it cannot be detected by the well-known dark amethyst-red colour which it imparts to borax before the blowpipe. But its presence is easily indicated by fusing it with caustic soda, which it colours green.

Sulphate of the Protoxide of Cerium is obtained by submitting crystallized bisulphate of the peroxide of cerium to a gentle heat. The salt swells somewhat, gives off water, sulphuric acid and oxygen, and is converted into a white porous mass of sulphate of the protoxide of cerium. When the heat is too great, the protosulphate loses somewhat of its acid, and then leaves on solution a white powder of basic protosulphate of cerium. The anhydrous neutral salt contains 57·39 per cent. protoxide of cerium, and is therefore = CeO, SO^3.

The ignited protosulphate dissolves readily in cold water, with greater difficulty in hot water. The best method of obtaining the protosulphate of cerium crystallized is to dissolve the ignited salt in cold water, and to warm this solution gradually. The hydrated sulphate of the protoxide of cerium crystallizes in fascicular and stellate groups of oblique four-sided prisms. As long as the crystals remain in the liquid they appear to possess a strong lustre, and to be transparent and colourless; taken out of the liquid, they quickly become opake and white. They contain 16·5 per cent. aq = 2 at.

The protosulphate of cerium combines with the sulphate of potash in various proportions.

Neutral Sulphate of the Protoxide of Cerium and Potash is formed when a solution of protosulphate of cerium is brought into contact with crystals of sulphate of potash, this latter always being present in great excess.

Sesquisulphate of the Protoxide of Cerium and Potash is obtained when concentrated solutions of protosulphate of cerium and 2 parts sulphate of potash are mixed together. A white powder is deposited, which contains 37·65 per cent. sulphate of potash; the formula 3CeO, SO^3 + 2KaO, SO^3 requires 38·22.

Bisulphate of Protoxide of Cerium and Potash is formed when the quantity of the sulphate of potash is still more diminished, and concentrated solutions of equal parts of protosulphate of cerium and sulphate of potash are mixed together. A white pulverulent precipitate is obtained, which consists of 67·78 CeO, SO^3, and 32·22 KO, SO^3.

Oxide of Cerium is obtained purest when basic sulphate of cerium is mixed with double its weight of carbonate of soda, the mixture ignited, and the salts edulcorated; the oxide so prepared has a dirty white yellowish colour; it does not dissolve in the weaker acids, and is not even attacked by concentrated sulphuric acid, which nevertheless easily dissolves the oxide of cerium containing lanthanium. To determine its amount of oxygen, 100 parts of the basic sulphate of the oxide of cerium were dissolved in sulphuric acid, the solution evaporated, and the acid sulphate of cerium ignited. The salt is thus converted into the protosulphate of cerium, and 4·159 parts oxygen have been disengaged. Since the 100 parts of basic sulphate of cerium employed contained 59·04 parts oxide of cerium, the oxide will be composed of 4·159 oxygen and 54·881 protoxide of cerium, or in 100 parts of—

	Found.	Atoms.	Calculated.
Cerium.....	79·185	1 = 1150	79·310
Oxygen.....	20·815	3 = 300	20·090
	100·000	1450	100·000

Bisulphate of the Peroxide of Cerium.—Basic sulphate of cerium dissolves readily in sulphuric acid, forming a yellow liquid, from which bisulphate of cerium may be very readily obtained crystallized in equilateral, six-sided obtuse prisms. The salt consists of—

Oxide of cerium....	36·36	36·98	1 = 1450·0	36·50
Sulphuric acid	38·00	37·21	3 = 1503·5	37·91
Water.....	25·64	25·91	9 = 1012·3	25·53
	100·00	100·00	3965·8	100·00

On submitting the salt to heat, it swells up somewhat, loses water, sulphuric acid and oxygen, and is converted into protosulphate.

Basic Sulphate of the Peroxide of Cerium.—The crystallized bisulphate of cerium cannot be dissolved in water without undergoing decomposition; the liquid becomes opake, and deposits the basic sulphate, while a portion of the salt remains dissolved in the free sulphuric acid. On heating the liquid, another portion of the salt which remained in solution separates in the state of the basic compound; but it is not possible to precipitate the whole of the oxide of cerium from the solution by boiling only. The basic sulphate of cerium is a fine milky precipitate, which unites to a light, coherent sulphur-yellow powder. It consisted of—

Oxide of cerium.....	58·785	3 = 4350·0	59·04
Sulphuric acid.....	27·500	4 = 2004·6	27·21
Water.....	13·715	9 = 1012·3	13·75
	100·000	7366·9	100·00

When the basic sulphate of cerium is ignited, it changes its yellow colour into a dirty white; it does not lose any sulphuric acid, but water and 2·1 per cent. oxygen. Water extracts from the ignited mass protosulphate of cerium.

Sulphate of Cerium and Potash.—When a solution of bisulphate of cerium is mixed with a solution of sulphate of potash, a lemon-yellow pulverulent precipitate is formed, which consists of—

Oxide of cerium	27·64	1 = 1450	28·23
Sulphuric acid	49·15	5 = 2505·8	48·79
Potash	23·21	2 = 1179·8	22·98

The salt becomes white on ignition, loses 11·7 per cent. sulphuric acid and oxygen, and is converted into sulphate of the protoxide of cerium and potash.

Prot-Hyperoxide of Cerium.—When nitrate of cerium is heated, an oxide is left behind, which contains more oxygen than oxide of cerium; on its conversion into protosulphate of cerium, it liberated 8·28 per cent. oxygen. It is therefore probably = $C^3 O^5$ or $C^2 O^3 + CO^2$.

Per-Hyperoxide of Cerium.—When the preceding oxide is dis-

solved in sulphuric acid, the solution diluted with 50 parts water, and boiled basic sulphate of cerium is thrown down. If now caustic soda be added to the boiled liquid, a brown precipitate is formed, which the author suspects to consist for the greater portion of hyperoxide of cerium. On drying, this precipitate remains of a dark brown; it has a glossy fracture; on ignition it disengages carbonic acid, which the oxide had absorbed from the atmosphere, water and oxygen, and leaves behind prot-hyperoxide of cerium. 100 parts of the precipitate, dried at 212° Fahr., afforded on ignition—

Prothyperoxide of cerium	73·75
Oxygen	3·40
Carbonic acid	11·59
Water	11·26

After subtracting the carbonic acid and the water, the per-hyperoxide of cerium would be composed of—

Cerium	74·60	1 = 575	742
Oxygen	25·90	2 = 200	258

Journ. für Prakt. Chem. for November.

Products of the dry Distillation of Tobacco.

Prof. W. G. Zeise, in Copenhagen, has submitted tobacco smoke and the products of the dry distillation of tobacco to an accurate chemical examination. He has found them composed of the following constituents:—A peculiar empyreumatic oil, *butyric acid*, carbonic acid, ammonia, paraffine, resin, water, probably some acetic acid, some carbonic oxide and carburetted hydrogen. M. Zeise has not been able to detect creosote in those products, which it would seem was not formed in this operation.—*Journ. für Prakt. Chem.*

Lead Cachexy:—The Poison detected by Chemical Analysis in the Brain and Lungs.

A man of fifty years of age, a house-painter of intemperate habits, had frequently suffered from lead colic, and was slightly affected with wrist-drop, from which however he had completely recovered. For two or three of his attacks of colic he was treated in the King's College Hospital. In December last this man was brought into the hospital, and placed under my care; he had had a severe epileptic fit, which ended in continued coma. In this state he was brought to the hospital, and soon had a second fit, also of epileptic character. After a few days he recovered considerably, but still showed evidence of much cerebral disturbance by a wildness of manner and incoherence of expression, which struck every one who saw him as resembling those which occur in delirium tremens. Opium and stimulants were highly beneficial to him, and we began to entertain hopes of his ultimate recovery. However, after the lapse of several

days he again became stupid; and now we noticed a remarkable fœtor of the breath, which at once excited suspicions as to the existence of gangrene of the lung. He sank quickly after this symptom showed itself.

I had from the commencement felt certain that the cerebral symptoms were, at least principally, the result of poisoning by lead. The *post-mortem* examination confirmed this opinion, and afforded other highly interesting information.

The brain was pale, much shrunken, and the gray matter of a very light colour. A good deal of subarachnoid fluid existed in consequence of the shrunken state of the cerebral convolutions. There was no disorganization of the brain.

The right lung, besides a large gangrenous cavity in its centre, exhibited a very extensive lobular inflammation, affecting the apex as well as the base of the organ. Many lobules were hepatized, others in incipient suppuration, and some were the seat of little abscesses. In all the inflammation appeared to have begun around a point, as a centre, and to have extended throughout the lobule; and in many of those in which the inflammation was in an early stage, I found in the centre of each a very minute blackish point, suggesting the notion that it might be some compound of lead entangled in the pulmonary tissue, and exciting inflammation around it. The appearances in this lung forcibly call to mind the description given by Cruveilhier of the effects consequent upon the injection of quicksilver into the veins. In those cases, the globules of mercury were the centres around which as many lobular inflammations took place.

It was ascertained, on chemical analysis, that lead existed in great quantity in the brain; and in the lung this metal was found in still greater proportion. There could be no doubt that the presence of the metal was the cause of the functional disturbance of the former organ, and of the disorganizing process in the other.—Todd's *Practical Remarks on Gout, Rheumatic Fever*, &c.

Action of Prussic Acid on Calomel and on Corrosive Sublimate.

When, according to M. Mialhe, prussic acid is poured over calomel, cyanide of mercury, muriatic acid and metallic mercury are first generated; but after longer contact, the muriatic acid for instance acts again on the mercury and cyanide of mercury, and finally a mixture is obtained of cyanide of mercury, corrosive sublimate, muriatic acid, prussic acid and metallic mercury; collateral products are ammonia and formic acid. Æther readily extracts the prussic acid and corrosive sublimate, and leaves behind the cyanide of mercury. Other salts of the protoxide of mercury undergo analogous decompositions by prussic acid and the alkaline protocyanides. M. Mialhe ascribes to this formation of cyanide of mercury the fact of several cases of poisoning having arisen from administering mixtures containing calomel and at the same time *Aqua lauro-cerasi*.

ANALYTICAL CHEMISTRY.

On the Behaviour of the Antimoniate of Potash towards the Earths. *By* M. WACKENRODER.

FROM my examination of the applicability of antimoniate of potash as a test for soda*, I was led to investigate its behaviour towards the alkaline earths, and also towards alumina; since from the frequent occurrence of the three latter bases in salts of potash and soda, the value of the antimoniate of potash as a test would be considerably diminished, if we remained unacquainted with its behaviour towards salts containing these earths.

The following are the results of my experiments. I need only add that the strength of the solutions were the same as employed in my former investigation.

Salts of Barytes.—Antimoniate of potash produces, in a solution of chloride of barium, a white, voluminous, flocculent precipitate of antimoniate of barytes, which does not alter its state of aggregation even after long standing. When the solution of the chloride of barium is very much diluted, the antimoniate of potash still causes a flocculent sediment; but the precipitate only forms on the addition of a sufficient quantity of the potash salt, from the antimoniate of barytes being soluble in an excess of chloride of barium. This clear solution deposits very few or no flakes within twenty-four hours, but there separates on the surface a small pellicle of a salt, which consists of roundish, adherent granules resembling fish-roe. It would therefore appear that this pellicle is produced by the carbonic acid of the atmosphere, and is consequently merely accessory.

Salts of Strontia.—Antimoniate of potash behaves towards a solution of chloride of strontium in nearly the same manner as towards chloride of barium. However, with a certain concentration of the liquid, and a certain addition of antimoniate of potash, there is formed in the voluminous precipitate an acicular salt, which appears under a magnifying power of 200 times to consist of fasciculi and tissue of needles. After long standing there is also formed on the surface of the liquid a fine crystalline pellicle, and some larger sandy granules are deposited on the sides of the test-tube. These larger granules appear under the microscope to have no crystalline surfaces, but to be formed quite distinctly of *concentric layers*. The flocculent precipitate dissolves readily in excess of dilute chloride of strontium; the liquid is nearly perfectly clear, and only deposits a few flakes after long standing, but a pellicle forms on the surface.

The aqueous solution of the sulphate of strontia is rendered opake by antimoniate of potash; after some time there is a slight flocculent precipitate, and a deposition of the above-mentioned minute granules on the sides of the test-tube. The precipitation of strontia by antimoniate of potash is one of the best means of detecting this alkaline earth.

* See this Journal, vol. i. p. 708.

Salts of Lime.—Antimoniate of potash immediately produces in a solution of chloride of calcium a voluminous flocculent precipitate, which does not become crystalline, and which redissolves to an almost clear solution in an excess of chloride of calcium. Very few flakes are deposited from this solution on its being allowed to stand exposed to the air, but a pellicle of minute crystals forms on its surface, which consists probably of biantimoniate of lime. It results hence that when only a little of the test is added to a dilute solution of chloride of calcium there is no flocculent deposit; but with a sufficient quantity of antimoniate of potash, even when the solution of the lime-salt is excessively dilute, there is a turbidness, and subsequently a flocculent precipitate, so that it would almost appear as if the sensitiveness of oxalate of potash towards salts of lime was even surpassed by that of the antimoniate of potash.

The aqueous solution of the sulphate of lime affords, immediately on the addition of antimoniate of potash, a voluminous flocculent precipitate, which undergoes no change in its state of aggregation even after long standing. The liquid deposits no crystals. The smallest quantity of lime in salts of potash, especially in the carbonate of potash, may be detected instantly by the antimoniate of potash from the opacity produced.

Salts of Magnesia.—Magnesia is thrown down from the aqueous solution of its salts, especially from that of the sulphate of magnesia, in a voluminous and flocculent state by the antimoniate of potash. The antimoniate of magnesia redissolves to an almost clear solution in an excess of sulphate of magnesia, but a few white flakes generally separate after standing. On this account no flocculent precipitate is produced in very dilute solutions of magnesia, except when a sufficient quantity of the test is employed; small quantities of magnesia are easily overlooked, even when the solution is but moderately dilute. Frequently however a crystalline opacity results on agitating the liquid, which might easily be confounded with that which is formed with salts of soda; when the solution is excessively dilute, so that no precipitate results on the addition of the test, small crystals are deposited within twenty-four hours in considerable quantity.

The crystals appear to be the neutral salt, since they do not form in an aqueous solution of carbonate of potash to which a small quantity of sulphate of magnesia has been added. Such a solution affords with antimoniate of potash a flocculent precipitate similar to the antimoniate of lime. The crystals are nearly insoluble in pure water, and but very slightly soluble in a cold dilute solution of carbonate of potash, sulphuret of ammonium, and sulphuret of potassium; they are rapidly decomposed by muriatic acid. Tersulphuret of antimony is therefore immediately produced when some alkaline sulphuret is poured on them, and an excess of muriatic acid is added.

The primitive form of the crystals is that of an oblique rhombic prism. When the crystals are allowed to form slowly in a moderately dilute solution of pure sulphate of magnesia, they are per-

fectly developed, and form a sandy powder of vitreous lustre, the prismatic form of which can easily be detected with the assistance of a good lens. Magnified 200 times, and with a good light, they appear perfectly transparent, well-defined crystals, which refract the light very powerfully. It will always be necessary to attend carefully to the crystalline form of the antimoniate of magnesia, when employing the antimoniate of potash as a test for soda; or else to assure oneself of the total absence of lime and of magnesia in a liquid by oxalate of potash and by basic phosphate of ammonia.

It should always be borne in mind, that on mixing the antimoniate of potash with salts of ammonia, precipitation takes place. A solution of the test in 100 parts of water gradually affords, with a moderately-dilute solution of sal-ammoniac, a considerable flocculent precipitate, which most probably consists of biantimoniate of ammonia.

Salts of Alumina.—Antimoniate of potash produces a voluminous flocculent precipitate in a solution of potash-alum, which re-dissolves to a clear solution in excess of alum; no crystalline deposit is formed, and only after very long standing of the liquid are a few flakes apparent at the bottom of the test-tube. When a dilute solution of alum is mixed with a *little* antimoniate of potash, the liquid remains clear, and is not rendered opake even after long standing.—*Archiv der Pharm.* for June.

PHARMACOLOGY.

On Madder. *By* M. Girardin, Professor of Practical Chemistry at the Municipal School of Rouen.

In commerce the name of *Lizari* has for a long time been restricted to the entire roots of the madder, while that of *Madder* is applied to the pulverized roots.

The Lizaris are very little employed for the purposes of dyeing, and there is hardly any but the Lizari of Avignon which is met with in the markets of France. The Lizari of Cyprus is actually of rare occurrence; that of Alsatia is never met with.

The powders called *madders* are distinguished according to their origin into *Dutch Madder*, *Alsatian Madder*, and *Madder of Avignon* or of the *Comtat.*

Up to the present time no one of the numerous works which have been written upon this subject, no work of Materia Medica or of applied botany, has given the history of these powders, nor the peculiar characters of each variety; I shall endeavour to supply this want by giving a detailed description of the three kinds of madder met with in commerce. My situation has enabled me to make a particular study of this important tinctorial product; and the following remarks are the result of many and various observations:—

1. *Dutch Madder.*

The Dutch madder, which was formerly extensively employed in France, has almost entirely disappeared from our markets, from the heavy duty which the government purposely put upon it, in order to maintain and encourage the cultivation of that of Alsatia and of the Comtat. This madder possessed a well-deserved reputation, and there is no doubt but that it would again be generally used, if the duty, which is equivalent to a prohibition, were to be reduced. The following are its distinctive characters:—Its odour is strong and nauseous; its flavour is sweet, with a mixture of bitterness; its colour varies according to the marks, and passes from a brown-red to an orange-red *.

In general its powder is stringy (*en paille*), that is to say, its state of division is sufficiently large to exhibit the structure of the root. It is coarser than the powder of the other kinds of madder, which might be attributed to negligence, since frequently portions of Lizari are met with which have not yielded to the grindstone. This coarse state of comminution however is no defect, since it prevents fraud. This powder appears greasy to the touch. Exposed to the action of the atmosphere, it readily absorbs moisture, and when, for the sake of ascertaining its quality, it is exposed to a moist air, its orange-red changes to a bright red, of a rich depth of colour. The Dutch madder *works* more than the others, according to the commercial term, *i. e.* it presents more decided modifications of colour by exposure to moist air.

Dutch madder is *stripped* or *not stripped*. In the first case, the roots have been freed from their epidermis, which gives greater brightness to the powder; in the second, they have been triturated without undergoing this operation, when the powder is of a more sombre colour. This madder cannot be used while fresh; it must be a year in the cask at least. After three years it is in full vigour.

The *pale* powder, or of a yellow aspect the first year, soon undergoes fermentation with age; the divided parts then unite with each other, agglomerate, and increase in volume to such a degree, that, after several years, the dilatation is so great that the bottoms of the casks present a very marked convex form. The madder is then so hard, that in order to take it out of the cask, a mallet or chisel must be used. This madder ferments more than the others.

It keeps several years after having attained its greatest tinctorial power (about three years), after which the layers which line the sides of the casks begin to lose their brightness; the madder assumes a pale brown colour, and it enters into decomposition. The progress of this is slow but certain; it subsequently becomes quite extinct, and the madder has a brown-red colour.

In its decomposition it may still be used for brown grounds or

* The red-brown tint is only applicable to the *mulle* madder of each kind. The term *mulle* or *billon* is applied to the inferior quality of madder. It is a mixture of the smallest roots, of the fibres, and of the epidermis of the large roots, of earth, and of the bran or refuse of the sieves.

colours; but when age has destroyed all the colouring principle, it can only serve as *mulle*.

The marks current in our markets are—

Mulle O.....	or	Mulle.
Superfine		Fine grappe.
Not stripped or stripped		Superfine grappe.

This word *grappe* (bunch) is employed when age has given consistence to the powder. The term *grappe* is used to designate its state of agglomeration.

This kind of madder formerly came from Holland in oaken casks of the weight of 600 kilogrammes.

2. *Alsatian Madder.*

This madder, which has replaced the Dutch in our manufactories, although it does not possess all its qualities, has the following characters:—

The smell is less decided, more penetrating than that of the preceding; taste less sweet, equally bitter; colour brown to bright yellow, according to the mark; state of division coarse. It easily absorbs moisture from the atmosphere; by long exposure it changes from yellow to a dark red; in use, however, it inclines more to yellow.

As is the case with the Dutch madder, it is not employed while fresh; it is in full vigour when two years old. It deteriorates sooner than the former; its fermentation is less decided; it grows very hard however in the casks, coheres to the very centre, and there is the same difficulty to extract it. The progress of decomposition is the same; the madder which has undergone this process can only be used for dark tints.

The Alsatian madder is never known by the denominations of *stripped* or *not stripped*, although the operation of *stripping* takes place. The marks alone distinguish the varieties. The marks known in our markets are—

O, Mulle.	SF, Superfine.
MF, Mi fine.	SFF, Superfine fine.
FF, Fine fine.	

The most generally used is FF.

SFF is nearly an exception to the method employed by the Alsatians in grinding, who are strict enough in their marks to be unwilling to prepare a very fine quality, which would be to the injury of the preceding.

The madder of Alsatia is packed in oaken casks or hogsheads of 600 kilogrammes, in half hogsheads of 300 kilogrammes, in quarters of 150 kilogrammes, and in barrels of 100 kilogrammes. All these hogsheads are similar in form, and only differ in size.

It is at Strasburg, Hagenau and Geisselbrunn that the so-called Alsatian madder is manufactured.

3. *Madder of Avignon.*

The madder of Avignon is most generally used at the present time, and even preferred to the other kinds, because the dyer and

cotton-printer find it easier, by using it, to vary the reds according to wish. It is especially since the peace of 1815 that the use of this madder has greatly increased.

Of all the kinds of madder this is the sort which has undergone the most modifications; I may say, almost the only kind in which variations have been made in the marks and in the quality. In Holland and in Alsatia the quality specified is generally conformable to the mark. In Avignon, on the contrary, each manufacturer has a mark to designate its quality; and the mark SFF, which with one is beautiful, is but middling with another. The result is, that the trader cannot trust to the mark alone, which presents a different tint in each manufactory. The madder of Avignon therefore can only be bought after having been spread out to view upon linen.

The characters of this powder are,—odour agreeable, slightly penetrating; taste sweetish bitter; colour either rose, bright-red or brown-red, according to the roots employed in the preparation and to the degree of mixture; state of division very fine; powder dry to the touch.

When submitted to the action of the atmosphere, it absorbs moisture less readily than the other species; however, it does not work less, and subsequently affords a pale or very dark red, according to whether the powder operated on was *rosy* or *palus*.

In Avignon they are not acquainted with the terms *stripped* or *not stripped* (*robée ou non robée*). There the word *épuration* is used. A madder is purified from 3, 5, 7 or 10 per cent., and even as high as 15 per cent. This mode of expression is pure quackery, for how is a root to be purified except by depriving it of its epidermis, and how can we suppose that the root may contain at will so much more or less of it as to require that the purification should sometimes be carried to 15 per cent.? We should have to suppose that the weight of the epidermis was to that of the root as 1 : 7, 10 or 15, which is not the case.

The best madder is made with the roots of the Palus. In Avignon the name of *Palus* is given to some tracts of land anciently covered with marshes; these lands, enriched by animal and vegetable remains, are eminently suited for the cultivation of the madder, and the roots they produce are almost all *red*, whilst other kinds of soils produce rose-coloured roots.

The powder from the Palus madder is of a dull and rather unsightly red, but on drying it becomes blood-red, which may be varied at pleasure. A small quantity goes much further than a larger quantity of the *rose-coloured* root.

The *rose-coloured* madder is made with the so-called *rosy* Lizaris. The powder is of a bright red, bordering a little upon yellow.

The madder, which is half *palus*, half *rosy*, forms a brilliant powder, which is well received in the market, and which affords very satisfactory results in dyeing. The brilliancy of the *rosy* madder mingling with the rich depth of the palus, produces a most beautiful red.

The madder of Avignon may be used immediately on leaving the mills; but the powder which has been preserved in casks for a year is decidedly preferable. It keeps well, and undergoes little or no fermentation in the casks; it does not cohere in a mass; after several years, however, it is decomposed with nearly the same symptoms as the other kinds: it is still used in this state. The small degree of fermentation evinced by this madder arises from its containing much less mucilaginous, saccharine, and bitter substances than the Dutch and Alsatian madder, for it is certain that the acid fermentation which is so energetically developed in the latter must be attributed to those substances.

Although pressed with great force into the casks, the madder retains a certain quantity of air between its particles, which in time acts upon the whole mass and gives it a uniform colour, by oxidizing the primitive yellow colouring principle and changing it into a red principle. This theory, advanced by M. Decaisne, very well explains why the madder powders are improved in quality by being preserved for a certain time in the casks*.

The drying of the roots in the stove has great influence on the tint of the madder of Avignon. If dried at too high a temperature, the powder is dull, without however losing in quality.

At first only two kinds of Avignon madder were known, the *yellow madder* and the *red madder*. The first has since disappeared, and the *rosy madder* is now substituted for it.

As to the marks, it is difficult to give positive information on the subject, especially since quackery has endeavoured to deceive by extraordinary names. Originally only the following marks were known:—

Mulle.
FF, Fine fine.
SF, Superfine.
SFF, Superfine fine.

These marks were put upon the casks without other designations. The tint alone decided to what sort of root the powder belonged. At present the madders are either—

Palus, or
Rosy, or
Half Palus, half rosy.

When it is wished to denote that a madder is all *Palus*, a P is added to the mark. The following are the actual marks:—

Mulle, without distinctive marks.

FF, SFF, SFFF — To each of these marks the letter P is added for Palus, R for Rosy,
EXTF — PP for Pure Palus,
EXTSF — RPP for Pure Red Palus.
EXTSFF — Half Palus, half Rosy, without distinction.

* Anatomical and Physiological Researches concerning the Madder. By M. Decaisne. 1 vol. 4to. Brussels, 1837.

According to these designations, it is by no means rare to find the absurd marks of

EXTSFRPP,

which is to be understood thus:—

Extra superfine fine pure red Palus.

It must be confessed that such absurdities can only exist in a country where fraud has made revolting progress. It often happens that the mark EXTSF, now used, is not equal to the old one of SFF.

The *extra fine* is especially manufactured with the heart or the ligneous part of the root. This mark gives less depth, because the ligneous part is less rich in colouring principle than the fleshy part or the bark of the root, but it affords a much more lively colour. The madders of Avignon are packed in deal casks of 900 kilogrammes in weight. The insides of these casks are generally lined with very thick pasteboard, in order to prevent contact with the air, which blackens the powders, causes them to appear less beautiful, and after a certain time destroys much of their tinctorial properties. Light also very quickly changes the colouring principle of these powders.

It is rather difficult to ascertain exactly the quantity of madder gathered each year in France, as well in Alsatia as in the ancient county of Venaissin.

In 1837 the crop of the Lizaris amounted in these districts to 1,200,000 kilogrms., which is equivalent to from 48,000 to 50,000 barrels, of which part was sent to the different places where it is consumed, as well within as without the country, conformably to the following table:—

	kilogrammes.
Rouen, Havre and Dunkirk	3,800
Antwerp	500
Genoa and Leghorn	183
London, Liverpool and Glasgow	3,760
London, Liverpool and Glasgow, 8000 bales of lizari, which represent	3,500
Hamburg	530
St. Petersburg	1,608
Odessa	110
Rotterdam	423
Trieste	205
New York and Boston	812
Mulhausen, Strasburg, Metz and Basle, for the consumption of Alsatia, Prussia, Switzerland, Bavaria, Austria, &c.	15,000
Total	30,481

There remained therefore of the harvest of 1837 at Avignon and in the department, from 18,000 to 20,000 barrels when the harvest of 1838 was about to be got in. This, although less than the former, amounted to between 36,000 and 40,000 barrels.

The manufacture at Avignon is always in a prosperous condition. The state of the customs shows, that in 1840 there was exported

from France 2,161,158 kilogrammes lizaris, which represent in value 1,620,869 francs, and 12,114,054 kilogrammes of madder (equal to 12,114,054 francs); that in 1841 there were exported 1,896,416 kilogrammes of lizaris (equal to 1,422,312 francs), and 11,840,886 kilogrammes madder (equal to 11,840,886 francs).

The importation of foreign lizaris and madders is very small, on account of the heavy duties. The lizaris chiefly come from the Levant by way of Turkey, the Barbary States, from Tuscany, the two Sicilies, and from Germany. The madders come especially from Holland and Belgium.

[To be continued.]

Scopolina Atropoides.

M. Lippich recommends the extract of this plant in cases of mercurial salivation, and it has been administered in numerous cases with success by Drs. Brenner and Felsach. Not more than 2 grs. should be given in a day, or it proves narcotic.

On the frequent Occurrence of Lead in Cochineal.

M. Dietrich, in a letter to Prof. Wöhler, mentions his having received a parcel of cochineal, which in appearance left nothing to be desired as to quality, but which had nevertheless been subjected to a gross sophistication. The white coating, for instance, was artificial, and contained so many granules of lead that they amounted to nearly 12 per cent. in weight. When the mixture was reduced to a very fine powder, and then carefully suspended, a bright metal remained behind. Since cochineal is frequently employed by pastry-cooks, the sophistication is highly dangerous; and this adulteration appears now to be very generally adopted, for all the samples of cochineal which the author examined proved to contain lead.—*Archiv der Pharm.* for November.

Adulteration of Potato Starch.

M. Dietrich draws attention to the fact of his having received potato starch mixed with comminuted fibre, which amounted to 50 per cent. of the starch; the goods were received from Magdeburg. The mixture of fibre prevented the employment of the starch in the fabrication of yeast for a distillery.—*Archiv der Pharm.* for Nov.

Adulteration of Jalap Root. By M. Ingenohl.

Sometimes brown, ragged, pear-shaped fragments are found mixed with the true jalap root, which resemble it very much externally, but are not so heavy, and are either soft and flexible, or readily broken when they have been roasted. In many pieces fibres may be distinctly perceived, and from this, as also from their sweet taste, they would seem to be dried fruit which had been immersed

in tincture of jalap, and have thus been rendered somewhat acrid to the taste. Similar adulterations have also been observed in articles sent under the name of jalap root from Bremen.—*Archiv der Pharm.* for November.

CHEMICAL PREPARATIONS.

New and advantageous Method of preparing the Bicarbonate of Potash and the Bicarbonate of Soda. By M. Behrens.

With a view of obtaining the acetate of potash I formed a solution of equal portions of carbonate of potash and of water. On gradually adding to it the acetic acid, I observed at first scarcely any disengagement of carbonic acid, and only subsequently, on adding considerably more of the acetic acid, did the liberation of gas commence suddenly with much vigour. There had however formed a precipitate, which amounted at least to half of the potash employed.

The precipitate was beautifully white, and presented a mass tolerably well crystallized, which, pressed in linen and washed with cold water, proved to be nothing else than pure bicarbonate of potash.

There are many œconomical methods, it is true, for obtaining this bicarbonate; but if it be considered that by the method just described this preparation is obtained as a secondary product, and that with half the trouble there is obtained at the same time the acetate of potash and the bicarbonate of potash, both of which are extensively used, I believe that I may recommend this new method, especially to chemical manufacturers.

After having separated the bicarbonate of potash which had been deposited from the liquid, it is requisite to add to this latter so much more acetic acid as is necessary to form the neutral acetate of potash.

The same method is adopted to obtain the bicarbonate of soda; it is necessary however to take a concentrated boiling solution of carbonate of soda before adding the acetic acid to it, because otherwise very little bicarbonate of soda would be precipitated, while when the solution is concentrated a large quantity separates, even while the whole is still over the fire.—*Journ. de Pharm.* for Dec. 1843.

Improved Method of preparing Chlorate of Potash. By Prof. Juch.

Pass chlorine gas into a mixture consisting of 1 lb. caustic lime, 1 lb. carbonate of potash and 8 lbs. of water, as long as there is any absorbed. In this manner two salts are obtained, which are very easily separated by crystallization; for the chlorate of potash crystallizes readily from the filtered solution, the chloride of calcium scarcely at all. In this method there is no loss of potash, in the state of chloride of potassium, which formerly amounted to nearly one-half.—*Journ. für Prakt. Chem.*

Medicina Magnesiæ.

According to M. Capitaine, the *Magnesia usta* is very frequently administered in Guadaloupe and in the West Indies in the dose of 8 grs., mixed with sugar and water, or syrup under the name of *Médecine de Magnesie.* The sugar is essential; probably being converted in the stomach into lactic acid, it acts upon the magnesia and dissolves it, rendering it one of the most valuable purgatives. M. Mialhe recommends that this mixture should be prepared in the following manner:—8 grms. *Magnesia usta* are triturated with some syrup, and then mixed with so much syrup that the whole amounts to 80 grms; to this are added 20 grms. *Aq. flor. aurantii.* This dose is taken at one time.—*Journ. de Therapeutique*, August.

Syrupus Antirachitus.

℞ Ol. jecoris Aselli	125	parts.
Extr. fol. nuc. Jugland	45	...
Mellis	735	...
Aq. distill.	6	...
Kali Iodidi	6	...
Syrup. cort. Chinæ	375	...
... simp.	1125	...
Essent. Anisi	240	...

Journ. de Chim. Med., 1843.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Observations on the Manufacture of Sugar. By Carl Hochstetter.

Since we know for certain that no other sugar than cane-sugar exists in the beet-root or in the sugar-cane*, the formation of molasses can only be ascribed to decompositions which the sugar undergoes in the course of its preparation. The molasses of the sugar-refiner do not consist, it is true, solely of modified cane-sugar; they contain salts, colouring and other substances, the nature of which have not been precisely characterized, and a large quantity of cane-sugar. Although impossible on a large scale to obtain more crystallizable sugar from them, yet, especially from the molasses of the beet-root sugar manufacturer, very considerable quantities of cane-sugar may be procured in a crystalline state on the application of animal charcoal and alcohol, without however it being possible to extract the whole. Soubeiran has examined various molasses with a polarizing apparatus, and has calculated their amount of cane-sugar at 50 per cent†. Ventzke has found still larger quantities, as much as 60 per cent. The entire quantity of molasses therefore which are obtained in practice cannot be regarded as the product

* See the author's previous observations on this subject, vol. i. pp. 692, 714.—Ed.

† After deducting the water which the molasses contain.

of decompositions, for some salts possess the property of entirely preventing the crystallization of the cane-sugar, and of forming with it a kind of molasses. The same influence is said to be exerted by the uncrystallizable sugars.

The author has shown that the cane-sugar of juice from the beet-root, made alkaline, on evaporation at a boiling temperature over a naked fire, is not changed, nor is it altered in the process of clarifying. In both these processes therefore the influence of heat contributes nothing to the formation of a new sugar.

The author has moreover shown that solutions of sugar may be directly modified at temperatures above the boiling point of water with the presence of nitrogenous substances; this occurs during the evaporation, when the sugar requires some protection, either lime or some free alkali. In the best-arranged manufactories, both for the preparation of beet-root sugar as also for refining colonial sugar, vacuum pans are employed for the boiling down, in which the temperature of the boiling solution of sugar never attains the temperature of boiling water; the influence of heat must be considerably modified. Soubeiran has also shown that the saccharine juices are not perceptibly altered by evaporation in vacuum.

Whether any considerable quantity of sugar is decomposed on evaporation, under the ordinary atmospheric pressure, by means of steam-heating or over a naked fire, the author leaves undetermined. On a large scale, the differences both in quality and quantity are very inconsiderable between the products of the various manufactories which carry on their evaporations and boilings in vacuum, and those in which they are performed carefully over a naked fire.

According to all that is known of the manufacture of sugar in tropical countries, the juice of the cane exhibits the property of running very readily into fermentation, favoured by the high temperature of the atmosphere, so that it may be admitted that a great portion of the original cane-sugar is already modified before the juice is submitted to any other operation. The bad sugars of the colonies likewise undergo, in their long transport, modifications which may be considered as analogous to a process of fermentation; sometimes the sugar is acid, probably containing lactic acid; sometimes it contains mucous or gummy products, but it always contains modified cane-sugar. When the cane-sugar comes to our refiners, it is treated with the greatest care, and boiled in vacuum, so that no sugar can be decomposed, and a portion of that which forms the mother-leys (syrup) is sugar in the act of change, when the syrups have been kept for some time in the refineries.

The juice of the beet-root would undoubtedly, in the high temperatures of the tropical countries, undergo decomposition more rapidly than the juice of the cane, because a considerably larger amount of substances which induce fermentation exist in it; fortunately however the time of manufacturing is during winter. Nevertheless, it may be observed, that the beet-root juice changes as soon as it leaves the cells of the plant, and the more readily the higher the temperature in the caves in which the roots have been preserved,

and the higher the temperature of the atmosphere. In good establishments it is not allowed to proceed to apparent changes, for the sap for instance to become acid and slimy, but it is frequently altered even without this sign. These changes are always connected with the state of the roots; in autumn, when the roots are worked up immediately after the harvest, the temperature of the surrounding atmosphere has no perceptible influence; but in January and February, it is commonly observed, in almost all manufactories, that with the appearance of thaw, therefore of a higher temperature, worse and less products are obtained; as soon as cold sharp weather again sets in, the same roots afford more and better sugar.

In the germinated beet-root, it is quite as impossible to detect a foreign sugar as in the fresh ungerminated plant; but the nitrogenous substances have undergone some change, and in spring these easily modify the juice, already at temperatures a few degrees above freezing point. We are not able to separate by means of lime the entire amount of nitrogenous substances from the juice; there still remain considerable quantities, varying according to the altered state of the roots. We know, further, that even alkaline clarified juice is susceptible of change under the influence of the atmosphere and other favourable circumstances, and that it may be entirely decomposed by a process of fermentation. Whenever the clarified or evaporated juice presents large surfaces to the action of the atmosphere at moderately warm temperatures, whenever it is allowed to stand for any considerable time, it is very liable to undergo decomposition. The changes do not cease even when the sugar is brought into the forms, for the first mother-leys (syrup), which consist for the greater part of cane-sugar, are, when left for some time exposed, constantly in the act of slow decomposition; the more dilute the syrup the quicker do these changes occur.

The opinion, therefore, that the decompositions of the cane-sugar take place solely under the influence of these nitrogenous bodies, supposing that the operations, if not with alkaline juices, are conducted in vacuum, appears to be correct; and that when the boiling is effected with care over a naked fire, the smallest portion of the changes is attributable to the higher temperature.

The saccharine juice is obtained from the beet-root in two ways—by pressure and maceration of the fresh roots, or by extracting the dried slices of the beet. With the present mechanical arrangements for the expression of the juice, this operation is effected so quickly that improvement appears impossible; but the becoming black of the juice indicates that some alteration is wanted. This change has, it is true, according to all experience, no ill effect; it is considered, on the contrary, as a sign of the good quality of the juice, but it also proves with what rapidity such alterations proceed. In most manufactories it happens however that the different quantities of juice are left for several hours in reservoirs, or that they are not well separated. Thin layers remain for a long time exposed to the air on the sides of the presses, of the reservoirs, and especially of the apparatus employed; these undergo decomposition, and being mixed

with the fresh juice, modify and spoil large quantities of it. The strainers and cloths of the presses constitute a far greater source of ferment. To avoid these evils is the best means to insure success.

Those who adopt the methods of maceration, mention as the principal advantage of their plan, that on boiling the sections of beet-root or the fresh beet-root mass, the albumen of the root is coagulated, thus preventing the fermentation of the sap, which destroys the results in the press method. This is however a great error.

On boiling the beet-root, only a portion of the nitrogenous substance is precipitated, and even lime acts only on one portion, forming insoluble compounds; a great portion, and indeed that very portion which induces most readily the changes described, remains dissolved in the juice. The action of heat has, it is true, very much modified the influence of this substance, and has even suspended it for some time; but it soon reacquires its power in a favourable temperature and in contact with the atmosphere. The beet-root requires to be at least six hours in the very best macerators, to be thoroughly extracted. An accurate separation of the quantities of juice obtained at different times is difficult to effect on a large scale, on which account some portions of the juice frequently remain for a considerable length of time under circumstances favourable to fermentation; they become changed, and finally draw the whole amount contained in the macerators into the process of their decomposition. On this account all methods of maceration hitherto proposed have failed.

Lime is now exclusively employed to separate the foreign ingredients contained in the juice of the beet. This body has no injurious action, but it does not answer completely, for it leaves in solution a quantity of substances, the removal of which it would be desirable to effect. Only under certain circumstances does it act injuriously; when, for instance, the juice, previous to being treated with lime or before evaporation, contain other kinds of sugar; for these are decomposed by the alkalies, and go to increase the quantity of the foreign matters already present, and which moreover are in part of a very colouring nature. But large additions of lime act injuriously, inasmuch as it becomes requisite to remove the lime previous to boiling; for which purpose either acids are necessary, which it is not desirable to employ, or animal charcoal, which is expensive. They also have an injurious action, from their decomposing the foreign sugars contained in the juice, colouring the cane-sugar with the products of their decomposition, and deteriorating the quality of the molasses. It is well in such a case, especially during evaporation, to keep the juice as little alkaline as possible, but to add during evaporation gradually so much lime that the juice remain alkaline.

According to the author's experiments, the evaporation of the alkaline juice in vacuum appears useless; according to his experience, on a large scale, the same juice afforded on evaporation in vacuum and in open evaporating pans down to 25° Beaumé, the

latter the best products of the two; and this was most decided with spoilt sap.

When clarified beet-root juice is evaporated in the vacuum pan at a temperature of from 158° to 176° Fahr., scarcely any perceptible precipitates are formed, consisting of minute suspended flakes, evidently from the temperature being too low for the foreign organic substances to be decomposed. No matter how alkaline the juice may be, nor how much foreign organic substances it may contain; no separations worthy of remark take place at this temperature. Such a juice therefore still contains after evaporation all the foreign substances in solution, the greater portion of which is separated on evaporation at higher temperatures. Evidently therefore the juice evaporated in open pans is purer than that evaporated in vacuum; and since neither in the one nor in the other case is any foreign sugar formed or cane-sugar decomposed, the first method must afford the best products.

We are thus able to explain why the advantages of evaporation in vacuum with inferior beet-root juices are less apparent, for such a juice contains a larger quantity of foreign substances in solution, which, isolated, form viscid and slimy substances, and these must prove very obstructive to the crystallization of the sugar. These substances are modified by the action of heat and the alkalies on being boiled under ordinary atmospheric pressure, lose their viscid and gummy properties, and at the same time those products of decomposition which, being insoluble, are no longer retained in the saccharine solution. The advantages which were expected to accrue by effecting all operations of boiling in rarified space, have consequently proved very deceptive.

Those modes of evaporation, in which the juice of the beet is made to trickle over heated surfaces, and thus to lose its water by being brought into considerable contact with the atmospheric air, are wholly to be rejected; the temperatures in these methods are in general too low to exclude the catalytic influence (if we may use such an expression) of the nitrogenous substances on the sugar, and also too low not to modify the sugar, even when the juice is alkaline.

Some systems of evaporation have also been employed, in which hot air has been driven through the juice, and the evaporation of the water effected in this manner. The œconomical advantages of such a method will not easily induce a manufacturer to adopt such a process. The alkaline solutions of sugar are, it is true, even in this case, not easily altered, supposing that the temperature of the evaporating liquid be near that of the boiling point of water.

Contrary to general opinion, M. Hochstetter has constantly observed, in operations on a large scale, that when evaporation is carried on at temperatures below 212°, more slimy products are obtained than at higher temperatures.

Since the saccharine juice should only contain, when inspissated for crystallization, as few foreign bodies as possible, as they all more or less prevent the formation of the crystals, the excess of lime which the juice generally contains after evaporation should be removed. The

employment of sulphuric acid for this purpose requires very great precaution, and moreover some quantities of gypsum remain dissolved in the liquid. Animal charcoal is too expensive for this purpose. Of late, therefore, it has been proposed to employ (and this has actually been carried into effect) the carbonic acid obtained by the combustion of coal. But since it is of advantage that the juice should be alkaline, the application of carbonic acid would appear to be only of use after evaporation had been effected, supposing even then that it were not open to objection in an œconomical point of view.

Animal charcoal for decolorizing, and indeed for removing foreign substances, both organic and inorganic, is the sole means which has hitherto been employed with advantage on a large scale. It answers its purpose completely, but unfortunately its high price sets a limit to its employment. It is scarcely imaginable that so many different foreign substances could be removed from the juice without any injury to the sugar, in any other manner than by an absorbent acting like charcoal.—*Journ. für Prakt. Chem.*, xxix. p. 41.

On the Preparation of Chromate of Lime. By Robert Oxland*.

The bichromate of potash has been for two or three years rather extensively employed in the bleaching of palm oil. By the process employed, the bichromate is converted into the muriate of chrome. In order to render this substance again available for the same purpose, it is converted into the chromate of lime in the following manner:—The muriate of chrome is at first mixed with small portions of oil, from which it is carefully separated by treatment with hot water, which is also required for the necessary dilution of the liquid.

Any free acid is in the next place neutralized by the careful addition of milk of lime, prepared by slacking newly-burnt lime with hot water. The neutral solution is then removed to another vessel, leaving any precipitated sulphate of lime.

From this solution the green oxide of chrome, associated with hydrate of lime, is precipitated by a further addition of milk of lime. The colourless supernatant liquor, containing muriate of lime, is removed, and the precipitate well-washed. The preparation of the precipitate is completed by the further admixture of the hydrate of lime required for the conversion of the oxide of chrome into chromic acid. The precipitate requires to be slowly dried; when dry it is brought upon a hot plate, where by exposure to a red heat it is eventually converted into the chromate of lime, containing an excess of lime of a very bright canary-yellow colour.

The chromic acid is obtained from this substance by precipitating the lime by sulphuric acid as sulphate of lime. The conversion is not effected until the moment of the exposure of the mixture to a red heat.

It is probable that the formation of the acid is due to the oxygen

* Original communication.

obtained by the oxide of chrome from the decomposition of the atom of water, a constituent of the hydrate of lime.

Regarding the oxide as a sesquioxide, $1\frac{1}{2}$ equivalent of oxygen is required for its conversion into chromic acid; but as the equivalent of lime combining with the chromic acid supplies only sufficient water for an atom of oxygen, half an atom additional is requisite. It has been found in practice that a slight excess above the $1\frac{1}{2}$ equivalent of hydrate of lime is absolutely necessary to the success of the process.

PATENT.

Patent granted to William Pontifex, Shoe Lane, London, *for an Improvement in treating Fluids containing Colouring Matter, to obtain the Colouring Matter from them.*

The improvement proposed under this patent is to concentrate the colouring matter contained in various fluids, and required for dyeing, printing, and other manufacturing purposes, by evaporating, or partially evaporating the fluid *in vacuo*; and thus obtaining a highly concentrated colouring extract, or dye colouring powder, without the colour being injured by carbonization, or other causes, arising from the ordinary method of applying heat.

The fluid is placed in an ordinary vacuum-pan, and heat having been applied thereto in the usual way, the exhausting apparatus connected with it is worked more or less rapidly, according as the steam which is to be drawn off is more or less rapidly disengaged, a good vacuum being always maintained. If, for instance, a decoction of logwood is the fluid under operation, it should not be allowed to remain in the vacuum-pan until it arrives at a viscid state; but when so much of the water has been evaporated as to reduce the remaining portion of the decoction to a state of hypersaturation, it should be drawn off and allowed to settle. The clear portion of the decoction is poured off, and returned to the vacuum-pan; the sediment is allowed to dry, and is put by in that state until required for use; or it may be first reduced to a fine powder in a mortar. Other fluids may be evaporated until they assume a viscid form; the extent to which the evaporation is carried depending upon the intended use of the colouring matter.

The feature of novelty claimed by the patentee is concentrating the colouring matter contained in fluids, and required for manufacturing purposes, by applying heat to, and thus evaporating, or partially evaporating, the said fluids *in vacuo*; whereby a highly concentrated colouring extract, or dye colouring powder, is obtained, without any injury to the colour from carbonization, or other damage, inevitably occasioned by the application of heat in the ordinary way; and it is also rendered more portable, as well as in a more pure state for use.—Sealed Jan. 28, 1840.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constitution of the Succinates. *By* M. Döpping.

From an analysis of a succinate of lead, M. Fehling was led to ascribe a bibasic nature to succinic acid. It would likewise appear to result from Fehling's researches on the sulpho-succinic acid, and the investigations of Cahours on the decomposition of succinic æther by chlorine*, that succinic acid is not $C^4 H^2 O^3 + HO$, but $C^8 H^3 O^5 + 3HO$, and that the so-called anhydrous succinic acid is analogous to the metaphosphoric acid. The author has carefully examined most of the succinates, and has found that we are *not* justified, from their constitution, in regarding succinic acid as polybasic.

The acid, as obtained in commerce, was still much contaminated with empyreumatic products, and was of a brown colour. Several methods were employed to purify it:—

1. *Treatment of the Aqueous Solution with Chlorine Gas.*—On evaporation, the acid separated in faintly-yellowish crystals, which could not be entirely freed from this last portion of colouring principle, either by repeated recrystallization or by frequent treatment with chlorine. The chlorine does not affect the constitution of succinic acid, however long it may be allowed to act upon it, either in the cold or with the application of heat.

2. *Digestion with Charcoal.*—This does not afford a perfectly colourless acid, even after frequent treatment. The charcoal takes up much of the acid.

3. The acid was heated to boiling *with* about four times its weight of moderately-*concentrated nitric acid*, and kept at this temperature for some time. When the liquid has been allowed to boil for about half an hour, the oil and colouring substance which adhered to the crude succinic acid are destroyed; and on conveying the contents of the retort and recipient into a porcelain dish, the succinic acid separates on cooling in perfectly white crystals, which are entirely free from smell. Nearly the entire amount of acid is obtained in the first crystallization. It is obtained free from nitric acid, which adheres pretty strongly to it, by recrystallizing it several times from water, and is then perfectly pure, forming colourless prismatic crystals, which, heated on platinum foil, volatilize without leaving any

* See vol. i. p. 682 of this Journal.

residue. No nitric acid could be detected in its aqueous solution by the protosulphate of iron or by metallic copper. The crystallized acid undergoes no change by exposure to the atmosphere; at 392° Fahr. it gives off a slight quantity of hygroscopic water, and then consists of 1 equivalent anhydrous succinic acid and 1 equivalent water, which may be replaced by bases; its formula is therefore $C^4 H^2 O^3 + HO$, and the atomic weight of the anhydrous acid (carbon taken at 75·85) = 628·35.

Succinic acid is just as little altered by nitric acid as by chlorine, even when the acid is employed in a concentrated state, and heat is applied. The purification of crude succinic acid by means of nitric acid was first indicated by Marceau, and recommended as the best method by Lecanu and Serbat.

The alkalies form with succinic acid neutral and acid salts, both of which are readily soluble in water and in aqueous alcohol. They support, with the exception of the ammonia salts, a tolerably high temperature (from 446° to 464° Fahr.) without being decomposed, and possess the remarkable property of dissolving in somewhat considerable quantities the potassio-chloride and ammonio-chloride of platinum, so that no complete separation of the bases can be effected by chloride of platinum, even from an alcoholic solution of the potash and ammonia salts. An alcoholic solution likewise takes up ammonio-chloride of platinum in such quantity that the liquid acquires a yellow colour. The alkaline succinates do not enter into combination with one another to form double salts. The alkaline earths afford with succinic acid only neutral combinations, which are in part soluble in water, partly not. No acid salts of the alkaline earths exist, any more than double salts of them with the alkaline succinates. Magnesia, which forms the transition from the alkaline earths to the so-called true earths, gives with succinic acid and potash a double salt. The magnesian group of oxides afford salts, in which the alhydrate water is wanting.

Succinic acid appears to form with the oxides of the so-called heavy metals only neutral and basic salts, in definite and constant proportions; at least those which hitherto have been considered as acid salts do not bear the character of chemical combinations. Some of the salts are soluble in water, others not. They all bear heating to 392° Fahr., some of them even to 446° and 464° Fahr., without being decomposed; the same is the case with the salts of the alkaline earths.

Neutral Succinate of Potash.—$KO\,\overline{S}^* + 2Aq$. When a solution of succinic acid is neutralized with carbonate of potash, and the ley brought to crystallization, this salt is obtained generally in imperfectly-developed crystals, the form of which cannot be determined. It deliquesces by exposure to the air, is soluble in alcohol, insoluble in æther, loses the whole of its water (16·2 per cent.) at 212°, so that heated up to 396° it undergoes no further decrease in weight;

* $\overline{S}$ represents an equivalent of anhydrous acid, as expressed by the formula $C^4 H^2 O^3$; H = 12·48.

when exposed to a higher temperature, it melts quietly without volatilization, being decomposed. It contains 40·39 per cent. potash; the formula requires 40·87 potash and 15·59 aq.

Bisuccinate of Potash.—$KO\,\overline{S} + HO\,\overline{S} + 4$ Aq. When a certain quantity of succinic acid is saturated with carbonate of potash, and as much acid again added to the neutral solution, regular crystals are obtained on evaporation, which are transparent, and form six-sided columns; exposed to the atmosphere, they gradually become opake, and effloresce on the surface; they dissolve readily in alcohol and water, colour blue litmus-paper red, and dried at 212° give off all their water of crystallization (18·07 per cent.). The salt may be heated to 446° without decomposition; it melts at a higher temperature, being decomposed with volatilization of a portion of the succinic acid. It contains 24·46 potash; the formula requires 24·49 potash and 18·67 aq.

Neutral Succinate of Soda.—$NaO\overline{S} + 6$ Aq. This salt is easily obtained in colourless transparent rhomboidal columns, when an aqueous solution of succinic acid is saturated with carbonate of soda, and the ley evaporated at a gentle heat. It does not easily part with its water of crystallization by exposure to the air, is readily soluble in water and in aqueous alcohol, behaves neutral towards litmus-paper, and loses at 212° the whole of its water of crystallization, viz. 39·85 per cent. It contains 22·92 per cent. soda; the formula requires 23·08 per cent. soda and 39·83 aq.

Bisuccinate of Soda.—$NaO\,\overline{S} + HO\,\overline{S}$ is obtained in the same manner as the corresponding potash salt. The salt separates in distinct flat six-sided crystals; it effloresces slowly by exposure to the atmosphere, loses its water of crystallization (32·68 per cent.) entirely, and behaves at a higher temperature like the corresponding potash salt. It contains 15·89 per cent. soda; the formula requires 32·33 aq. and 16·06 soda.

Neutral Succinate of Ammonia.—$NH^4O\,\overline{S}$ or $AdH^2O + \overline{S}$. The author obtained this salt by supersaturating succinic acid with strong solution of caustic ammonia, and evaporation of the ley over caustic lime beneath a bell-glass, in the form of transparent six-sided prisms, which had a slight acid reaction, gave off ammonia by exposure to the atmosphere, were easily soluble in alcohol and water, did not effloresce, and contained—

		Atoms.		Calculated.
Carbon	31·71	4 =	303·40	31·76
Hydrogen	7·85	6 =	74·87	7·83
Nitrogen	18·50	1 =	177·03	18·54
Oxygen	41·94	4 =	400·00	41·87
	100·00		955·30	100·00

Bisuccinate of Ammonia.—$NH^4O\,\overline{S} + HO\,\overline{S}$ is obtained when the solution of the neutral salt is evaporated at a gentle heat, or when a certain amount of succinic acid is neutralized with ammonia, and an equal quantity of acid again conveyed into the solu-

tion and evaporated. The salt crystallizes readily in transparent well-developed six-sided prisms. The salt is easily soluble in water and in alcohol, has an acid reaction, is not altered by exposure to the air, and loses scarcely a few per cent. at 212°; but on being heated to 284°, the salt volatilizes, being partially decomposed. It consists of—

		Atoms.		Calculated.
Carbon	35·54	8 =	606·80	35·77
Hydrogen	6·73	9 =	112·32	6·64
Nitrogen.....		1 =	177·03	10·44
Oxygen		8 =	800·00	47·15
			1696·15	100·00

Succinic acid does not form a crystalline double salt containing potash and soda in definite proportions. Whether there exists a double salt of soda and ammonia in definite proportions was not ascertained.

Succinate of Barytes.—$BaO\,\bar{S}$. Succinate of soda immediately produces in a concentrated solution of chloride of barium a white crystalline pulverulent precipitate, which soon subsides and is easily edulcorated. When the solution of the barytes salt is dilute, the precipitate is formed only after some time, more quickly if the liquid be heated, or when a little liquid is added to it in which succinate of barytes is suspended. The salt behaves neutral, is very difficult of solution both in water, succinic acid, and potash, easier in hot acetic acid, and very readily in dilute muriatic and nitric acids; it is insoluble in alcohol and in ammonia. Heated to 392°, the salt loses but a few millegrammes without undergoing any change in its constitution. It contains 60·49 BaO (calculated 60·36).

An acid succinate of potash does not exist. When chloride of barium is added to a solution of bisuccinate of soda, no precipitate is formed in the cold; but on warming and evaporating the liquid, a white crystalline powder separates, which after edulcoration and drying has the composition and properties of the neutral salt.

Succinate of Strontia.—$SrO\,\bar{S}$ is prepared like the barytes salt, and forms a white powder, which is sparingly soluble in water, readily in acetic acid, and is anhydrous. It contains 50·21 strontia (calculated 50·74).

Succinate of Lime.—$CaO\,\bar{S} + 3$ Aq. When a solution of neutral succinate of soda is added to a moderately-concentrated solution of chloride of calcium, no change is perceived; but after standing for some time, distinct acicular crystals separate, which behave neutral towards litmus-paper, dissolve, but not easily, in water and in acetic acid, are taken up in large quantity by a solution of succinic acid, dissolve readily in nitric and muriatic acids, and are insoluble in alcohol. The salt loses its water of crystallization when heated to 212°, with the exception of a small quantity, far less than an equivalent; the whole is expelled between 248° and 266°, so that it decreases no more in weight when heated to 392°. It afforded 26·01 aq. and 26·74 lime; the formula requires 26·93 lime and 25·54 aq.

The neutral succinate of lime dissolves readily in a solution of succinic acid on the application of heat. On cooling, a large quantity of shining, transparent, well-developed crystals separate from the liquid. They possessed an acid reaction, dissolved with difficulty in water and in alcohol, being rendered opake by the latter on the surface; they are not altered by exposure to the air. The salt, digested repeatedly with alcohol and dried at 392°, had however quite the same composition as the neutral salt.

The succinates of the alkaline earths do not afford double salts with the alkaline succinates. When recently precipitated carbonate of lime is dissolved in bisuccinate of soda and the solution evaporated, succinate of lime separates in crystals of the form of the neutral salt, from which the succinate of soda may be removed by edulcoration with water and alcohol.

The bisuccinate of potash behaves in the same way.

[To be continued.]

On the Atomic Weight of Zinc. *By* P. A. Favre.

The experiments published by M. Jacquelain on the determination of the equivalent of zinc*, in which the author expresses his conviction that the number 414 obtained by him is a minimum, which would inevitably make zinc an exception to the series of multiples of hydrogen, has induced me to undertake the present investigation. I have analysed several samples of oxalate of zinc, prepared with the greatest care, and of the purity of which I was thoroughly assured. The second method adopted was to ascertain the quantity of water decomposed, in order to oxidize a known weight of pure zinc.

The experiments by the first method furnished the following numbers for the equivalent of zinc:—

				Mean.
412·58	412·25	413·36	412·45	412·66,

which lead to 33·01 for the equivalent of zinc, taking that of hydrogen as unit. The numbers arrived at by the second method, taking 12·5 as the equivalent of hydrogen, were—

			Mean.
412·27	411·77	412·42	412·16.

These figures plainly represent a multiple of the equivalent of hydrogen by the number 33, and agree very well with those obtained by the first method. The equivalent of hydrogen being 1, that of zinc will be represented by 32·991, which is very close to the entire number 33.—*Comptes Rendus*, Nov. 20, 1843.

On the Non-occurrence of Lactates in the Blood.

As is well known, Prof. Liebig is opposed to those who have recently (M. Lehmann in particular) asserted the presence of lactic

* See this Journal, vol. i. p. 89.—Ed.

acid in most of the normal juices of the frame, and in general to the important part which they assign to it. He denies that lactic acid can be formed in the normal vital process from starch, &c., and places the views respecting the physiological importance of lactic acid in the same category with the earlier opinions on humus, &c. In accordance with this opinion, his pupil, M. Henderling, ridicules the idea of lactic acid acting as the conveying medium of phosphates. Several other of Liebig's pupils have also investigated this subject. M. Haidlen, in his researches on milk*, found that the carbonates contained in the ashes of the milk could not have proceeded from lactates, for when fresh milk is coagulated by means of dilute sulphuric acid and filtered, the whey evaporated to the thickness of a syrup, the residue evaporated with alcohol, the solution diluted with 3 parts water, then digested to saturation with freshly-precipitated carbonate of barytes, and sulphate of zinc added to the filtered solution, not a trace of lactate of zinc is obtained. M. Henderling has also recently shown that no lactic acid exists in the gastric juice, and the present investigation demonstrates the absence of lactates in the blood.

2 lbs. of ox-blood, scarcely cold, were freed by beating from fibrine, diluted with 4 times the quantity of water, mixed with hydrate of lime in excess, and then boiled until the whole of the coagulable constituents were entirely separated; after standing for some time, it was filtered, and the perfectly clear, almost colourless solution evaporated over a moderate charcoal fire, and when the liquid became more concentrated, over the water-bath until nearly dry. The liquid became gradually of a darker colour, and the residue had acquired an orange-yellow colour. This was repeatedly extracted with alcohol of 0·833 spec. grav., the alcoholic solution filtered, and sulphuric acid, which had been diluted with alcohol, added gradually, in order to separate the bases, so long as any precipitate was formed. The filtered solution, which contained, besides the sulphuric acid, the acids of the salts dissolved in alcohol, was digested with recently-precipitated carbonate of lead, until every trace of acid reaction had disappeared. The whole of the lead was removed from the filtered solution by a current of sulphuretted hydrogen, again filtered, and after it had been somewhat evaporated, diluted with a sufficient quantity of water, and gently heated, under constant stirring, with recently-prepared carbonate of zinc, and filtered while hot. The liquid containing the salts of zinc was evaporated to dryness on the water-bath, the pulverized residue extracted with alcohol, filtered, and the residue washed with alcohol. The liquid which passed through was very darkly coloured by extractive substances, and presented the appearance of a solution of biliverdine or chlorophylle. The residue, together with the filter, was boiled with water and again filtered; on the filter there remained a brownish-black pulverulent substance, resembling in appearance humus. The filtered solution was evaporated to the thickness of a

* See this Journal, vol. i. p. 427.—Ed.

syrup, and a portion placed in a small glass to crystallize; another portion was mixed with strong alcohol. If lactate of zinc had been present, there would have been obtained in the first case crystals, and in the second alcohol must have produced a precipitate; neither of which however occurred.

In other experiments, made with twice the quantity of blood, Henderling digested the alcoholic liquid which had been precipitated with sulphuric acid after dilution with water, with carbonate of barytes instead of with carbonate of lead, and added sulphate of zinc to the filtered solution containing the barytes salts as long as any precipitate was formed, evaporated the filtered solution to the thickness of a syrup, and placed it under a bell-glass by the side of sulphuric acid to crystallize; some small crystals were formed; the residue dissolved in alcohol.

M. Henderling likewise found no lactic acid in the blood obtained by venesection from a patient afflicted with pneumonia. He likewise made two experiments with blood, to which he had previously added a very small quantity of lactate of soda, and succeeded each time in obtaining decided crystals of the lactate of zinc. Calves' blood, sheep's blood and ox-blood gave ashes free from carbonic acid; they contained therefore no lactates.—Liebig's *Annalen.*

Simple Method of detecting Fibres of Cotton in Linen Textures. *By* Dr. R. Böttger.

After discussing the various methods hitherto employed, which are considered to be fallacious and unsatisfactory, even the microscopic test, the author proposes to employ a solution of equal parts of caustic potash and water, which produces at a boiling temperature a very decided yellow colouring of the linen fibre, while the cotton remains nearly colourless, or at the furthest so slightly yellow that the two may readily be distinguished by the naked eye without the least chance of deception. The examination is effected in the following manner:—About a square inch of the linen under examination is placed in the mixture of equal parts of potash and water, which has been raised to a violent state of ebullition, left two minutes in it, then removed with a glass rod from the silver or porcelain crucible, pressed gently, without previously washing it in water, between a double layer of white bibulous paper, and then from six to ten fibres gradually detached from the weft and warp edges. It will be seen immediately which fibres are cotton and which linen; the former being white or of a pale yellow, while the latter have acquired a dark yellow colour.

The test in question can of course not be applied to *coloured* textures.—Liebig's *Annalen* for September.

ANALYTICAL CHEMISTRY.

On the respective Value of the different Tests for the Detection of a Diabetic State of the Urine. *By* Dr. Golding Bird.

In the treatment of a disease so intractable and fatal as diabetes too generally proves, it becomes of essential importance to detect the first deviation from health. The earliest evidence of this, in the disease in question, is, as is well known, to be sought for in an examination of the urine, as a saccharine condition of that secretion is at least the most constant, if not the necessary, accompaniment of almost every phase of diabetes mellitus. It must not be supposed, however, that the existence of traces of sugar in the urine is indicative of the necessary presence of a confirmed diabetes; for it is beyond all doubt that small quantities of this principle may occasionally exist as the result of a depraved state of the primary or secondary assimilative processes. Still, as far as experience has extended, it has shown that such a condition of the urine must be regarded with great anxiety as a most suspicious symptom; as one which, at least, points out the existence of a most deranged condition of the functions of the stomach, and one which may, in all probability, if its cause be unchecked, be the forerunner of one of the most intractable diseases falling under the province of the physician.

It is true that in advanced diabetes, where the disease has become confirmed, and the system has suffered severely from its depressing influence, the increased quantity of urine, coupled with its high specific gravity and its general physical characters, will at once lead to the detection of the disease. Every one who has attended much to the pathology of the urine must have, however, met with cases of tolerably well-marked diabetes, *quoad* the general symptoms, in which, nevertheless, neither the quantity nor specific gravity of the urine would have by themselves been sufficient to lead to a suspicion of the true nature of the disease. A remarkable illustration of this fact occurred in the person of a young woman, who, in the past summer, was a patient in Guy's Hospital (in Dorcas ward), under the care of Dr. Barlow. She had previously been a patient of my own, and then presented well-marked constitutional symptoms of diabetes, with the exception of the absence of the excessive thirst and diuresis. This girl was twenty-eight years of age, but had never menstruated. The peculiar state of the tongue, which resembled a piece of raw flesh, and the harsh skin, induced me to examine the urine. The density of this fluid was but 1·022, scarcely above the average, and she passed but from 3 to 4 pints in twenty-four hours. I however found that it contained a large proportion of sugar. In a few weeks the quantity increased to 8 or 10 pints in twenty-four hours, and she ultimately fell a victim to confirmed diabetes. There is at this moment a man about sixty years of age in the hospital (Naaman ward), labouring under diabetes, who, when he first came under my care among the out-patients, attracted my attention by his

melancholic expression and harsh skin. On inquiry, I found that he passed but from 3 to 4 pints of urine in twenty-four hours, and the specific gravity did not exceed 1·024. It was, however, loaded with sugar. In this case the diuresis, or excessive discharge of urine and its high density, did not appear until some weeks after I had detected the presence of the disease. I have had, for nearly four years, a patient occasionally under my care (a green-grocer residing in Goswell Street) with diabetes, who, when first I saw him, had neither diuresis nor increased density of the urine; and these symptoms did not appear until some months after, although the urine was strongly saccharine the whole time. I need not multiply references to cases of this kind, as no doubt can exist as to the presence of diabetes, for at least some weeks, in cases where the indications afforded by the general symptoms appear to be negatived by what, on a very superficial view, may be taken for a healthy condition of the urinary secretion. Of course, the question of the probable presence of sugar can at any time be solved by chemical analysis, but this involves a considerable expenditure of time, as well as an amount of tact in investigations of this kind not always at the command of every practitioner; and hence the importance of possessing some test of the presence of sugar easy in its application and satisfactory in its indications.

1. *Hüpefeld's Test**.—Place 4 oz. of the suspected urine in a glass exposed to the sun's rays, and add about 6 drops of a tolerably strong solution of chromic acid. In a few minutes the mixture, previously orange red, becomes brownish, and soon after assumes a bistre-brown colour, if sugar be present. These changes take place much more quickly if the mixture of urine and chromic acid be gently warmed before exposure to light.

This test depends for its action upon the deoxidizing power of the sugar, by which the chromic acid is reduced to oxide of chromium; for, after warming the mixture, the addition of a few drops of *Liquor potassæ* produces a copious deposit of the green oxide. As pure chromic acid is prepared with great difficulty, I endeavoured to find some preparation which might replace it, and found that, by making bichromate of potash into a paste with sulphuric acid, and boiling the magma with not quite enough water to dissolve it, a solution was obtained, which, when decanted from the crystals formed during cooling, contained enough free chromic acid, or rather of a combination of this with sulphuric acid, to exhibit all the changes with saccharine urine above described. In using this solution, enough should be added to the suspected urine to give it a full orange colour, without which the subsequent changes will not be perceptible.

There is an important objection to this test which renders all its indications liable to serious fallacy, depending upon the fact, that all urine containing a normal proportion of colouring matter deoxidizes chromic acid; and consequently urine, whether saccharine or

* Journal für Practische Chemie, vii. 42.

not, will partially convert this acid into oxide. This change certainly does not occur so readily in non-saccharine urine as in a diabetic state of that fluid, but still is sufficiently marked to prevent Hünefeld's test being regarded in any other light than a fallacious one.

2. *Runge's Test**.—Allow a thin layer of the suspected urine to evaporate on a white surface, as the bottom of a white plate, and, whilst warm, drop upon the surface a few drops of sulphuric acid, previously diluted with 6 parts of water. With healthy urine, the part touched with the acid becomes merely of a pale orange colour, from the action of the latter upon the colouring matter of the urine; whilst if sugar be present the spot becomes deep brown, and soon black, from the decomposition of sugar by the acid, and consequent evolution of carbon. This test is stated to be so delicate, that 1 part of sugar dissolved in 1000 of urine can be readily detected; and even when mixed with 2000 parts the indications are tolerably distinct.

Regarding the sources of fallacy to which this test is liable, I may mention the presence of albumen, which causes the acid to assume a tint nearly resembling that produced by sugar. There is also a peculiarity in its action, which I have more than once had occasion to observe, namely, that if the urine be evaporated so as to be capable of being drawn into threads, it scarcely produces any change of colour on the addition of the acid until heat is applied. It is however a much more trustworthy test than the last, although certainly far inferior to the following.

3. *Trommer's Test.*—This, which is the latest test suggested for the detection of sugar, was proposed by Trommer of Berlin, and received the sanction of Professor Mitscherlich†.

Add to the suspected urine contained in a large test-tube, a few drops of a solution of sulphate of copper; a very inconsiderable troubling generally results, probably from the deposition of a little phosphate of copper. Sufficient *Liquor potassæ* should then be added to render the whole strongly alkaline; a grayish-green precipitate of hydrated oxide of copper falls, which, if sugar be present, wholly or partly redissolves in an excess of the solution of potash, forming a blue liquid, not very unlike the blue ammoniuret of copper‡. On gently heating the mixture nearly to ebullition, the copper falls in the state of sub-oxide, forming a red and copious precipitate. If sugar is not present, the copper is deposited in the form of black oxide.

This test is founded on a fact long known, but not previously applied to the detection of sugar, of the power possessed by some organic matters of reducing oxide of copper, as well as some other oxides, to a lower state of oxidation. It certainly is the most deli-

* Poggendorff's Annalen, band xxxiii. s. 431.

† An account of M. Trommer's method of detecting and distinguishing gum, dextrine, grape-sugar and cane-sugar, was published in the Philosophical Magazine for March 1842.—Ed. *Chem. Gaz.*

‡ Rose's Analytical Chemistry, by Griffin, p. 119.

cate of all the chemical tests hitherto proposed for the detection of sugar in the urine, and will readily detect it in diabetic urine, even when very largely diluted.

It is important in using this test that no more of the solution of sulphate of copper be used than is sufficient to afford a decided precipitate on the addition of the *Liquor potassæ*. If this precaution be not attended to, a part only of the black oxide will be reduced to red suboxide, unless a very large quantity of sugar is present, and thus the indications afforded by this test will be rendered indistinct.

In his remarks on this test, Dr. Simon observes that the presence of the urea and ammoniacal constituents of the urea may, in some cases, interfere materially with its indications. To avoid this, he directs the suspected urine to be evaporated to a syrup, and digested in pure alcohol. The alcoholic solution, being decanted, is agitated with dry carbonate of potash; and on being allowed to repose, it separates into two layers, the upper consisting of the alcoholic, and the lower of the alkaline fluid. A small quantity of a solution of sulphate of copper is then added, and the whole being warmed, a yellow or yellowish-brown precipitate occurs in the lower layer if sugar is present. I very much doubt whether this refinement of the test is ever necessary in practice, and it certainly has the objection of requiring a long time and a tedious manipulation for its completion, which is quite opposed to the character of *a test*. As directed by Trommer, his test can be applied to urine in a few minutes, and its indications are most satisfactory.

4. *Test of Fermentation.*—The development of the vinous fermentation on the addition of a little ferment or yeast to a fluid, has long been applied as a test for the detection of sugar. It was successfully employed by Professor Leopold Gmelin of Heidelberg*, for the detection of sugar in the animal fluids after the ingestion of amylaceous food. Dr. Christison has, I believe, the merit of particularly suggesting the application of fermentation for the discovery of a diabetic state of the urine.

When a little yeast is added to healthy urine, and exposed to a temperature of about 80°, no other change occurs for some time, except the development of a portion of carbonic acid mechanically entangled in the yeast. When sugar is present in the urine thus treated, it soon becomes troubled, a tolerably free disengagement of bubbles of carbonic acid takes place, and a frothy scum forms on the surface of the fluid, which evolves a vinous odour. These changes take place with great rapidity, even when the quantity of sugar present is very small. If the evolved carbonic acid is collected, the quantity of sugar in the urine may be determined by measuring it, as a cubic inch of the gas very nearly corresponds to a grain of sugar.

In certainly the great majority of specimens of diabetic urine, it is not necessary to add yeast to excite fermentation, providing a sufficient temperature be employed. This indeed has been stated to be

* Recherches Expérimentales sur la Digestion. Paris, 1826. Part 1. p. 202.

the exception, but from my own experience I can assert, that I have never yet left a glassful of diabetic urine upon a chimney-piece, when there is a fire in the grate, without having ample evidence of the development of fermentation within twenty-four hours. This test is certainly one of the best that can be employed, and is not subject to any obvious source of fallacy. It is however not so useful as Trommer's, as it cannot be appealed to at the moment, and requires time for the development of its indications.

5. *Test afforded by the Growth of Torula.*—It is a remarkable fact, that if the smallest proportion of sugar exists in urine exposed for a few hours to a temperature above 70°, and a drop of the fluid (taken from the surface) be examined under the microscope, numerous very minute ovoid particles will be discovered. In the course of a few hours more these become enlarged, and appear as distinct oval or egg-shaped vesicles, which soon become developed into a confervoid or fungoid vegetation, identical with that which appears in ordinary saccharine fluids when undergoing the vinous fermentation. In hot weather I have detected the oval spores of the *Torula diabetes*, as the organic production is termed, in diabetic urine within a few hours after its being passed; and for the last two years I have constantly relied on their appearance as the indication of the presence of sugar in urine. I can scarcely conceive an error arising from mistaking other organic particles for these spores, as the latter are always oval or ovoid, whilst all other of the organic particles developed in the urine are circular. As soon as the torula has appeared, vinous fermentation rapidly proceeds, and hence any possible inaccuracy, arising from mistaking other particles for the spores, becomes corrected.

The advantages of this test are the facility with which its indications are observed by the microscope with an object-glass of one-seventh or one-eighth-inch focus, and the certainty of any possible fallacy being corrected by the subsequent development of fermentation. It is however less convenient than Trommer's, in consequence of the time required before its indications can be observed.

I have excluded from this list of tests that of Bouchardat*, depending upon the circular polarizing power of the urine, as it is difficult in application, requires an expensive apparatus seldom at hand, and moreover has its indications seriously interfered with by the colour and imperfect transparency of the urine.

I have more than once had my attention directed to the probable presence of diabetes, by observing on the patient's trowsers white spots, arising from drops of urine having dried upon them. These spots consist of minute patches of dry sugar, and are readily removed by brushing. This, although it cannot be regarded as an actual indication of the presence of sugar, is nevertheless useful as a leading question in investigating the patient's history.

In conclusion, I would remark, that excluding Professor Hüne-

* Described in my 'Lecture on Urinary Deposits.' Vide Med. Gaz., 1843, p. 683.

feld's chromic test as too liable to fallacy to be of any practical value, the other tests, arranged according to the accuracy and convenience of their indications, may be thus placed:—1st, Trommer's copper test; 2nd, Growth of torula; 3rd, Development of fermentation; 4th, Runge's sulphuric test.

The profession must remain greatly indebted to Trommer for putting it in possession of a test for the presence of sugar in urine, so easy in its application, and so distinct in its indications, with the additional value of requiring but a few minutes for its employment. —*London Medical Gazette.*

PHARMACOLOGY.

On Madder. *By* M. Girardin, Professor of Practical Chemistry at the Municipal School of Rouen.

[Continued from page 20.]

4. *New Commercial Products derived from Madder.*

Since 1836 two new products occur in commerce, which are destined to replace madder in the operations of dyeing and calico-printing. One is known by the name of *garancine*, the other by the name of *colorine*.

A. The *garancine* is a more or less clear chocolate-coloured powder, without any decided smell or taste; it does not impart any colour to the saliva or to cold water even by long contact.

This garancine is nothing further than the *charbon sulphurique* of MM. Robiquet and Colin*, deprived of every trace of acid. A patent was taken out on the 26th of March 1828, by MM. Lagier, merchant, and Robiquet and Colin, Professors of Chemistry, for the manufacture and sale of this new product. As the specification which contains the description of the process of manufacture has never been published in any scientific work, I think it right to notice it in this place.

"The problem to be solved," say the patentees, "is to obtain the whole of the colouring matter of the madder free from the foreign bodies which tarnish its lustre, and retain it in combinations different from those which it ought to contract with the mordants; now the madder in its natural state contains colouring matter in various conditions. Thus in the dyer's bath it separates into two portions, one of which is either dissolved or suspended in the water, whilst the other remains fixed in the ligneous residue. In treating the exhausted residue, which is generally considered worthless, by the method described below, a quantity of colouring matter, at least equal to that first extracted from it, is obtained. Besides, the portion which the water carries with it, either in solution or in suspension, is far from being attracted by the mordant of the stuffs immersed in it.

* Société Industrielle de Mulhausen, t. i. p. 162.

A great part remains in the bath, in combination with some substances which retain it with sufficient energy to prevent it from combining with the mordants beyond a certain limit."

The following is the process proposed by them :—"The madder is immersed in from 5 to 6 parts of cold water, and allowed to macerate all night, in order that the portion of the colouring substance which dissolves at first may have time to subside; the whole is then thrown on to linen strainers, and when the liquid has passed through, the grounds are pressed; they are then immersed again in the same quantity of water, pressed, and this operation repeated once more. After these three washings, which serve to remove a green substance, besides sugar, mucilage, and other soluble substances, the grounds, still moist and well crushed, are mixed with sulphuric acid equal to half the amount of madder first employed; it is, however, requisite that this acid should be diluted more or less with water according to the temperature; this is done when it is about to be employed, in order to turn to account the heat set free by the mixture. The acid thus diluted is poured quite hot over the madder; it is then agitated as rapidly as possible, and when the mixture is thought to be well effected, the temperature is raised to 212° Fahr., and maintained for about an hour. At the end of this time the substance is again mixed with a suitable quantity of water, filtered, and washed on the strainers until the liquid passes off perfectly insipid. It is then pressed, dried, and passed through the sieve.

"In this operation the acid has undergone no alteration; it has merely become weaker and charged with some calcareous salts, which does not prevent its being employed in the manufacture of sulphate of soda. The first washing-water might also be turned to account, since it contains much sugar, which might easily be converted into alcohol."

Garancine was first introduced into commerce by the house of Lagier and Thomas of Avignon, towards the year 1829, who had bought the process and the patent of Robiquet and Colin; but this product did not meet with success in the market. The neutral state in which it was delivered not affording any correction to the calcareous waters ordinarily used in our Rouen print-works, and the action of their alkali on the colouring principle not being properly understood, the experiments which were made with it on a large scale were far from corresponding to those made with smaller quantities, and threw it into great discredit. It was not until later (in 1832) that the same house in Avignon, assisted by the advice of chemists, again commenced some trials, the results of which proving satisfactory, led to the belief that its use might become of importance. At this epoch, however, the madder-prints in vogue, being very dark and requiring a strong dye, could not be produced with garancine; the great quantity of colouring matter which they required prevented its use on account of its price; but in 1835 the issue of certain kinds of coloured prints requiring very bright colours, again drew the attention of manufacturers to garancine, and it was generally adopted and approved of.

Many persons, foreseeing how important its consumption might become, started establishments for the manufacture of it on the expiration of Robiquet's patent granted to Lagier and Co. Want of experience in this process caused these first manufacturers to obtain but imperfect products, and many soon left off; but shortly after, some persons, profiting by the experience of their predecessors, again took it up, and there are now from twelve to fifteen manufacturers of garancine at Avignon and one or two in Alsatia.

The manufacturers of Avignon employ only the madders of the Comtat; those of Alsatia are, it is said, obliged to add a small quantity of the former to the madder which they grow, in order to increase the quantity of colouring matter of their garancine.

From 1839 this substance began to be generally employed in several of the principal print-works of Rouen, among others by M. Schlumberger-Rouff, who manufactured the garancine which he used according to the following process:—

After having ground the already pulverized madder on a table by means of a thick wooden rolling-pin (such as is used by pastry-cooks), it was placed in a leaden basin, then moistened with a little water and half its weight of sulphuric acid of 1·834 sp. gr. poured over it, whilst two men continually stirred the mass with shovels, walking around the basin. When the burning (*brûlage*) was ended it was washed five or six times in barrels, the product drained upon linen, and then dried in a chamber heated by steam. It was afterwards ground in a water-mill, made upon the plan of pepper or coffee-mills. This garancine was very acid, and could not be used for violet colours. It cost 3 francs 75 centimes the kilogramme.

Originally garancine was worth 6 francs the kilogramme. For the last three years, the current price, without distinction whence it came, has been from 4 francs 50 centimes to 5 francs the kilogramme, with a discount of 6 per 100.

Up to the present time it has not been possible to class garancines according to their quality. Each manufacturer seeks to obtain the best products with regard to the quantity of colouring matter, and also with regard to the brightness of the tints; but the impurity of the first matters, and the neglect of trifling circumstances which the manufacture requires, often cause the products of the same manufactory to vary considerably. In trade garancines are met with which afford four times more colouring matter than the madder which was employed to obtain them, whilst others give but two and a half.

This want of regularity is as much dependent on the degree of richness of the madder employed, as on the operations necessary in the production of the garancine; there is so much danger of burning the madder too much or too little, that it is quite impossible to produce an identical garancine during a year. In great manufactories it is hardly possible to make fifteen to twenty barrels which shall be nearly alike; for which purpose it is even necessary that the whole mass of roots required should be treated at one time. In

general good garancines possess three times as much richness of dye as the good madders.

The same mode of classification has not been adopted for the garancines as for the madders; the former are only distinguished by the names of the manufacturers.

The garancine, both of Rouen and Alsatia, is packed in casks of from 200 to 300 kilogrammes. That of Avignon is expedited in casks, lined interiorly with blue paper, and with the jointures coated with tar.

During the last three years the consumption of garancine has been pretty regular; it may be calculated at from 1600 to 1800 barrels a year from Avignon, and from 400 to 600 barrels from Alsatia.

Before the introduction of this product into our manufactories, the yearly consumption at Rouen was from 3200 to 3500 barrels of Avignon madder, and about 1000 of Alsatian. For the last three years not more than about 2000 barrels of Avignon madder have been consumed, and 200 barrels from Alsatia. This diminution of nearly half the consumption of madder is more than compensated by that of the garancine and the Lizaris. The consumption of these last has however been almost nothing for five or six years; it may be valued at from 500 to 600 bales of every growth a year.

The following is the behaviour of garancine towards solvents:—

Cold distilled water	After 24 hours of contact it has only assumed a pale yellowish colour.
Distilled boiling water	Acquires a pale reddish-yellow tint.
Cold calcareous water	After 24 hours it is less coloured than with cold distilled water.
Boiling calcareous water	A somewhat paler tint than with distilled boiling water.
Cold lime water	After 24 hours the tint is paler than that with distilled boiling water, and than that with boiling calcareous water.
Water acidulated with sulphuric acid	Takes, after some hours, a slightly greenish-yellow tint.
Water acidulated with hydrochloric acid	Id., a rather darker tint.
Cold distilled water acidulated with nitric acid	Id., a rather darker tint, and the blackish-gray powder becomes of a brownish-red, resembling madder become brown by age.
Cold distilled water acidulated with acetic acid	Becomes faintly yellow.
Acetic acid of 1·0704 spec. grav.	Acquires, after several hours, a beautiful reddish-yellow colour.
Caustic ammonia	Becomes red immediately, and after 24 hours the liquor is strongly coloured crimson-red, so intense that it is no longer transparent in a great mass.
Water slightly alkalized by ammonia	Immediately assumes a beautiful claret-red colour.
Caustic soda	A dark reddish-brown colour.
Water charged with carbonate of soda	Acquires quickly a bright reddish colour of Burgundy wine.

Cold alum water	Becomes almost immediately of a chrome red colour.
Boiling alum water	Acquires immediately a dark red colour, and upon cooling deposits flakes of the same colour, but paler.
Alcohol of spec. grav. 0·863.....	Assumes rather quickly a slight reddish-yellow colour.
Hydrated æther	Id., id.

Dyeing with garancine is effected in just the same manner as with madder. It is more advantageous however to raise the bath at once to 113° Fahr., and then gradually to 167° or 176°. Garancine only yields its colour to the tissue impregnated with the mordant at a boiling temperature. The water of the bath acquires no colour even after ebullition, which always terminates the dyeing with garancine.

The mordants are the same as those which are employed for dyeing with madder.

For certain colours in which there is no violet, sumach is sometimes added to the bath to the amount of about a third of the garancine employed. At other times, for red grounds for instance, the pieces are quercitronned before garancing, which imparts much brightness to the red, but renders the violet gray.

The proportion of garancine used in dyeing calico prints varies considerably according to the intensity of the tints and the quantity of colour required by the pattern.

When the garancines are neuter and the waters are calcareous, which is general in Normandy, they must be corrected by adding a variable proportion of sulphuric, acetic or oxalic acid to the bath. 1 centilitre of sulphuric acid of 1·028 to 9 litres of water, or 15 centigrammes of oxalic acid to a litre of water, are about the quantities employed. When sumach is added no acid is employed.

There are some garancines which are badly washed and acid, and to which it is therefore necessary to add chalk or alkaline carbonates, in order to get rid of the too great excess of acid, which would be injurious; but chalk and alkalies are avoided as much as possible.

The great advantage of garancine is that it does not *charge* the white, and that the bleaching of the stuffs dyed with garancine is reduced to a mere nothing. When a very pure white is not required, it suffices merely to beat and sufficiently clear the pieces after the garancing. When a perfect white is required, the pieces are passed through bran for fifteen or twenty minutes. Hot water or bran are the only means used for clearing them. In this respect therefore garancine possesses a great advantage over madder, which covers all the whites, and which renders it necessary to use soap, and to clear them more or less after the process of dyeing.

The tints obtained with garancine are generally more brilliant and lively than those with madder. The *red* is vivid, of a carmine colour of extraordinary purity, whilst the madder red placed by its side is always somewhat yellow or of a fawn colour and dull, but on the other hand fuller. The *puces* and *garnets* made with garancine are much more velvety than those dyed with madder. The *violets* are not so pale and delicate and gray as with the latter. All the

tints are weaker, and cannot so well bear soaping; they also require great care in the clearing, and resist less the action of the atmosphere and of the sun.

All the garancines however do not afford tints of equal richness and brilliancy. Some kinds produce a beautiful red, but a bad violet colour; other kinds afford a magnificent puce or violet, while the red is dull brown.

Garancine was first employed in the calico print-works of Normandy. The Alsatian works refused to use this product for a long time; they only began to employ it about two years ago, in imitation of the calico-printers of Rouen.

M. Leonard Schwartz of Mulhausen has recently sent into commerce garancine prepared from the residue of madder which has been already used for dyeing. This matter, which he very improperly calls *garanceux*, is of much less value than the good Avignon garancine. $3\frac{1}{2}$, and even 4 parts, are scarcely equal to 1 part of the latter. It costs 2 francs 25 centimes the kilogramme.

B. The *Colorine* of commerce is the residue from the distillation of the alcoholic liquid obtained in the treatment of the *charbon sulphurique* with spirits of wine. The residue, which consists of *alizarine*, still impurified with a little fatty matter, is in the form of an extract when withdrawn from the retort. It is diluted with a little water and pressed, in order to separate the fatty matter from it as much as possible. When dry it is reduced to powder. This is Robiquet and Colin's* *alcoholic extract of charbon sulphurique*, which MM. Lagier and Thomas of Avignon brought into the market in 1836 at 75 francs the kilogramme.

This product is in the form of a very fine powder of a yellow-ochre colour, without any decided smell or taste; moistened, it stains the fingers strongly of a yellow colour, but it hardly colours saliva. It presents all the chemical characters which Robiquet and Colin assigned to their alizarine.

The expectations which had been entertained by these skilful chemists, as early as 1827, as to the possibility of using alizarine for obtaining colours of application, were realized in 1837 by M. Pariset of Rouen, who was then chemist in the works of MM. Feer, Dolffus and Company of Dieppdalle, and formerly pupil of M. Chevreul; and simultaneously in 1838 by M. Gastard, chemist to M. Stackler, and M. Daniel Fauquet-Delarve, of the print works at Deville. Colorine dissolved in ammonia, and the liquor being thickened with gum, affords, in fact, when printed on calicoes with aluminous mordants and exposed to steam, red and rose colours, which are by no means inferior to those obtained with madder dyes. A patent for fifteen years was taken out on the 24th of November 1837, by M. Stackler, for the carrying out the processes of M. Gastard; but the high price of the colorine of MM. Lagier and Thomas prevented their adoption in the print-works. The same was the case

* See MM. Robiquet and Colin's Memoir (Bulletin de la Société Industrielle of Mulhausen, i. pp. 177, 178 and 181).

with regard to the processes of M. Daniel Fauquet, who obtained in large quantities more intense and richer reds than those of M. Gastard. M. Fauquet's processes possessed another advantage, in so far as he was able to cause his red to *re-enter* (*rentrer*) upon black grounds dyed with logwood and other dyes, and as this red did not require so many clearings as that of M. Gastard to obtain vividness and brilliancy. M. Fauquet manufactured a large number of prints with applied red and rose colours, both in England and Scotland, but the enormous price of the primitive matter prevented his continuing. The Society of Emulation of Rouen, on my report, decreed medals of encouragement to MM. Gastard and Fauquet in 1839, for being the first to convert an experiment of the laboratory into an operation of the arts, and showing, in an indisputable manner, the justice of MM. Robiquet and Colin's presuppositions, viz. that it is possible, and even advantageous, to manufacture on a grand scale solid colours direct from the madder.

In 1840 M. Grelley and I undertook to investigate carefully the possibility of the practical application of the pure alizarine of Robiquet, a problem of the greatest consequence, since the *Société Industrielle* of Mulhausen proposed in 1834 a premium of 19,900 francs, to be raised by subscription amongst the principal dyers and calico printers of France, for the *discovery of a red of application from madder*, the price of a pot of the colour (containing 2 litres) not to exceed 10 francs*. This premium, which was continued until 1839, was never gained, and has been withdrawn. These facts show the great difficulty of the question. MM. Grelley and I have at last been able to solve it, by obtaining colorine at a price which allows of its being generally employed in producing red and rose colours of a good tint. We have described our processes in two *sealed packets*, deposited in the *Archives de l'Académie des Sciences*, dated 24th June 1841. We have since brought our processes of extraction to greater perfection. Our product is of as good a tint as the best reds obtained in the ordinary method of dyeing; it bears all the customary clearings, and since it is far more brilliant even in its natural state, it more readily yields to the action of the clearings than the ordinary madder-reds. Used in very small quantities, it resists the strongest clearings that are employed for Turkey red, which generally requires an excess of colouring matter. This product may be used with the greatest facility. It is mixed with weak ammonia, and left in it to swell; it is then thickened with gum-water, or with gum in powder, and applied to the tissue. The operations it requires after its application only consisting in a simple steaming and rinsing with pure water, it may be printed in every case with all the other ordinary steam colours, provided it is not intended to be cleared. The preparations preliminary to its application allow of its being applied to black grounds, or others obtained with matters of weak tint. It can be used of different degrees of

* Bulletin de la Société de Mulhausen, vii. p. 394.

strength on the same stuffs, and it is thus possible to obtain tints from a pale red to the very darkest red.

We have applied it on black and white grounds, which up to the present time were injured in the ordinary operations of dyeing. We have also applied it with catechu, when the clearing required was merely a simple soaping.

[To be concluded in our next.]

Influence of Season on the Activity of Narcotic Plants.

At a recent meeting of the Royal Society of Edinburgh, Professor Christison related a series of experiments instituted by him with a view of determining the influence of season on the activity of the poisonous narcotic plants of the family *Umbelliferæ*, of which the following is an abstract:—

The plants belonging to this family are for the most part aromatic and stimulant, and destitute of poisonous properties. In four species only have narcotic properties been unequivocally recognised, viz. *Conium maculatum*, *Œnanthe crocata*, *Cicuta virosa* and *Æthusa Cynapium*; but these are universally held to be highly energetic.

1. The *Conium maculatum*, Common Hemlock. No accurate information is yet possessed as to the influence of season on the activity of this species; for all investigations on the subject are vitiated by the uncertain strength of its preparations, and the ignorance which prevailed till very lately as to the conditions required for securing their uniformity. The author has found by experiment, as Professor Geiger had already been led to conclude, that every part of the plant is poisonous,—the root, the leaves, and the fruit; and that the root is least active, the leaves much more so, but the fruit most active of all. The root is commonly held to be most active at Midsummer, when the plant is in full vegetation and coming into flower; but this belief is founded only on a single, and not altogether conclusive experiment made by Professor Orfila. The author found this part of the plant to be so feeble at all times, that its respective energy at different seasons could not be satisfactorily settled. The expressed juice of twelve ounces of roots had no appreciable effect on a small dog at the end of October or towards the close of June; but an alcoholic extract of six ounces at the beginning of May killed a rabbit in thirty-seven minutes when introduced into the cellular tissue. The leaves are commonly thought to be most energetic when the plant is coming into flower at Midsummer, and to be very feeble while it is young. The author finds it to be probable that the leaves are very active at Midsummer; but he has likewise observed, that they are eminently energetic in the young plant both at the beginning of November and in the month of March, before vegetation starts on the approach of genial weather; thirty-three grains of a carefully prepared alcoholic extract, representing one ounce and a third of fresh leaves, killed a rabbit in nine minutes when introduced into the cellular tissue. The frnit is most active when it is full-grown,

but still green and juicy; it then yields much more of the active principle Conia than afterwards, when it is ripe and dry. The author added, as a fact contrary to general belief, that he had found the ripe seeds of hemlock and an alcoholic extract of the leaves to sustain no diminution in energy by keeping, at all events for eight years.

2. *Œnanthe crocata*, Dead-tongue. This species is universally considered to be the most deadly of all the narcotic *Umbelliferæ*. Many instances of fatal poisoning with its roots have been published during the last two centuries in the various periodicals of Europe. It has repeatedly proved fatal in two hours; and a portion no bigger than a walnut has been thought adequate to occasion death. Fatal accidents have occurred from it in England, France, Holland and Corsica. The root would seem from these cases to be the most active part; but few observations are on record as to the effects of the leaves, and none as to the fruit. The root appears from these cases to be very active in all seasons,—at least at the beginning of January, the end of March, the middle of April, June and August.

The author proceeded to inquire carefully into the effect of season upon this species, as it grows wild in the neighbourhood of Edinburgh; but he was surprised to find that every part of the plant in this locality is destitute of narcotic properties at all seasons. The juice of a whole pound of the tubers, the part which has proved so deadly elsewhere, had no effect when secured in the stomach of a small dog, either at the end of October, when the tubers are plump and perfect, but the plant not above ground, or in the month of June, when it was coming into flower; and an alcoholic extract of the leaves, and that prepared from the ripe fruit, had no effect whatever when introduced into the cellular tissue of the rabbit under the same conditions in which the common hemlock acts so energetically. By a comparative experiment he ascertained, that tubers collected near Liverpool, where one of the accidents alluded to above happened in 1782, acted with considerable violence on the dog; and he briefly noticed some experiments made at his request by Dr. Pereira with the *Œnanthe* of Wernich, showing that there also it is a powerful poison to the lower animals. Climate seemed to the author to furnish the only adequate explanation of these extraordinary differences; yet the plant grows in all parts of Scotland with great luxuriance.

3. *Cicuta virosa*, Water-hemlock. This species has been also held to be a deadly poison ever since an express treatise on its effects was published by Wepfer in 1716; and repeated instances of its fatal action have been observed since, and some of these very recently, in Germany. The root is the only part which has given occasion to accidents: it has proved fatal in two hours and a half. Nevertheless this plant too seems innocuous in Scotland, or nearly so, although, like the last species, it grows with great luxuriance. The juice of a pound of the roots, collected at the end of July while the plant was in full flower, produced no narcotic symptoms; and the only effects observed, namely efforts to vomit, might have arisen from the operation which is necessary to secure the juice in the stomach. An alcoholic extract of the leaves collected at the same time, and a simi-

lar preparation made with two ounces of the full-grown seeds while still green and juicy, had no effect whatever when introduced into the cellular tissue of a rabbit, except that inflammation was excited where the extract was applied.

4. The author has not yet had an opportunity of trying the effects of the fourth species, *Æthusa Cynapium*, or Fool's-parsley.

CHEMICAL PREPARATIONS.

On the Protiodide of Mercury, and its Applications. *By* M. Mialhe.

According to the author's opinion, an insoluble medicine can only become active by being decomposed, or by the intervention of the acids contained in the stomach, or of the free alkali in the intestinal juice, or lastly, by being rendered soluble by the soluble salts which occur in all the organs of digestion. According to him, calomel is of itself perfectly inactive; it operates only in so far as it either contains portions of corrosive sublimate, or is converted into this in the stomach. Now since these conditions are not always the same, the effects produced by calomel vary considerably. The protiodide of mercury is in this respect perfectly analogous to calomel; its action is on the whole weak and mild, but when sometimes it produces far more considerable effects, this is owing, according to M. Mialhe, to its either containing considerable quantities of the periodide mixed with it, or to its being administered in combination, or contemporaneously with iodide of potassium, which, as is well known, immediately produces a decomposition of the protiodide of mercury into periodide and metallic mercury. To be assured therefore of the mild action of the protiodide, it is requisite not to administer iodide of potassium either contemporaneously or just before or after its employment, and secondly, to use a preparation free from the periodide.

According to Berthemot's method, adopted by the French Codex, in which iodide and mercury are triturated together with some alcohol in the requisite proportions to form the protiodide, the preparation always contains periodide, of which it is very easy to be convinced by testing the alcoholic extract with sulphuretted hydrogen. The quantity of periodide varies considerably; according to Thierry it may amount to 9 per cent. Two varieties of the protiodide of mercury are met with, one greenish-yellow and neutral, the other yellowish grass-green and basic. The latter is easily obtained by triturating 100 parts of mercury with only 50 instead of 62 parts iodine; it is this latter which most frequently occurs; it contains far less periodide than the neutral preparation made according to the Codex, and is therefore preferred. The protiodide of the Codex may however be easily freed from any periodide by edulcorating it with

hot alcohol until the latter is no longer rendered opake by sulphuretted hydrogen. This should never be neglected, and physicians would do well always to prescribe protiodide of mercury which has been washed with alcohol.—*Bull. de Thérap.*, xxiv. pp. 357–359.

Employment of Veratrine in Rheumatic Paralysis. *By* Dr. Knapp of Berlin.

A young girl, eleven years of age, was attacked after a cold with paralysis of the right arm. She had been afflicted with this disease four weeks when she was admitted into the hospital. She then related that two years previously she had been seized with this affection, which had only given way at the end of two months.

This child, who had a very good constitution, had the right shoulder lower than the left; the movements of the right arm were executed slowly and without energy, so that the hand of this side could not even be used to convey the food to the mouth.

The use of hot baths was prescribed, and the application of a blistering plaster to the diseased shoulder. After having allowed suppuration to continue for eight days without success, it was suppressed, and the use of veratrine resorted to according to the following formula:—

℞ Veratrine..... 0·25 centigrms.
Lard ..... 30·00 grms.

Mix into a homogeneous ointment.

This was applied morning and evening, the frictions lasting for a quarter of an hour, the dose for each friction being about the size of a bean. The application excited in the diseased arm a sensation analogous to that produced by pricking with a pin, and in three weeks the arm had recovered all its motive faculties.—*Gazette des Hôpitaux* for November 1843.

Ergotine.

In a note addressed to the French Academy, M. Bonjean states, that since he has succeeded in freeing the ergotine from the poisonous principle* which rendered the employment of the ergotized rye so dangerous, several physicians have extended its use. It has been employed with success in Paris in some cases of chronic affections of the uterus, and in Turin in chronic and acute bronchitis.—*Comptes Rendus*, Dec. 11, 1843.

Febrifuge of M. Metzinger.

The success which a preparation compounded by me, and administered in the form of pills, has constantly met with for several years in the treatment of intermittent fever, induces me to publish the formula.

It is thus administered:—6 pills immediately after the access,

* See vol. i. p. 550 of this Journal.—Ed.

6 more three hours after the first dose, and a third dose three or four hours before the return of the fever. The access once stopped, the patient continues to take only two doses daily, each of 4 pills, one in the evening and one in the morning for three or four days, after which the doses are successively reduced to 3 and to 2 pills. This dose is for a person of a good constitution; it should be reduced according to the age, sex and state of the patient:—

Cinchona in powder	15 grammes.
Subcarbonate of potash	4 ...
Carbonate of ammonia	2 ...
Tartrate of potash	4 ...
Golden sulphuret of antimony	2 ...
Extract of buckbean	4 ...
Extract of wormwood	4 ...

Extract of parsley in sufficient quantity to form a pillular mass, to be divided into pills of 50 centigrammes. A few days' treatment suffices for recent and simple fevers, but in more serious cases it is necessary to employ the entire dose of 120 pills in order to prevent relapse.—*Journ. de Pharm.* for December 1843.

Eau de Bergamot (*Eau de Cologne*), *according to* L. Giseke.

8 quarts of alcohol of 0·833 spec. grav.,
6 ounces of oil of bergamot,
3 ... ... of cedra,
½ an ounce of oil of cloves,
½ ... ... of cassia,
½ ... of orange flowers,
1 ounce of Alcohol Vanillæ,

are mixed together. The *Alcohol Vanillæ* is prepared by digesting 1 part of comminuted vanilla with 12 parts of absolute alcohol for six or eight days, and then filtering. The alcohol must be perfectly free from fusel oil, and the oils must be of the best quality.—*Archiv der Pharm.* for October.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

New Methods of Acidimetry, and for testing the Commercial Value of Manganese Ore. By Drs. Fresenius and Will.

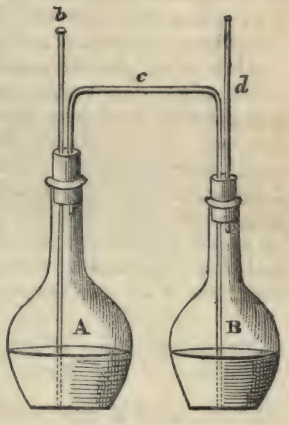
[In a former Number* we published the authors' process for ascertaining the commercial value of potash and soda, and then promised to give on some future occasion the other methods proposed for ascertaining the strength and value of acids and manganese; since the publication of that article, however, the excellent work from

* Vol. i. p. 636.

which our article was an abstract, has been carefully translated by Mr. L. Bullock; and we have therefore confined ourselves, in the present instance, to a mere outline of the processes, referring those readers who may wish for more information on the subject to the work itself.—Ed.]

Examination of Acids.

The acid is weighed off in the flask A (taking of sulphuric acid 0·911, of nitric acid 1·23, of muriatic acid 0·83, of citric acid 1·32, of tartaric acid 1·5, of acetic acid 1·16 grms., or any higher multiple of these numbers, according to the degree of dilution, for instance with vinegar 60 or 100 times the quantity); the requisite quantity of water is then added so as to fill the flask one-third; upon which 4 to 5 grms. of pure crystallized bicarbonate of soda is filled into a glass tube closed at one end, which is suspended by means of a silk thread in A; B is then provided with sulphuric acid, as described in the article on testing soda and potash; *b* is closed, the apparatus counterpoised, and the carbonate of soda allowed to fall into the acid. The sulphuric acid in B serves in the present instance to retain the moisture.



At the close of the experiment, A is warmed and the carbonic acid drawn out by suction at *d*. The loss in weight in centigrammes, divided by the number with which the normal quantity enumerated above for each acid had been multiplied, gives the per-centage of anhydrous acid.

Examination of Manganese.—2·98 grms. of finely-pulverized manganese are weighed off (after the sample has been freed, when necessary, from earthy carbonates by means of dilute nitric acid), and 6·5 to 7 grms. neutral oxalate of potash (or 5·5 to 6 neutral oxalate of soda) are placed in the flask A, and water added until the vessel is about one-third full; B is filled, as usual, with sulphuric acid. The whole is counterpoised, and some of the sulphuric acid made to pass over by suction, as in the examination of potash, until no more carbonic acid is disengaged, and *no* black powder remains at the bottom of the vessel A. The loss in weight in centigrammes divided by 3 gives the per-centage of peroxide of manganese. If it is desired to know at the same time how much acid is required to decompose entirely any given manganese ore, and how much of this acid is uselessly consumed by other ingredients, the following plan is adopted:—So much ordinary sulphuric acid is weighed off in A as shall amount to 5·47 grms. anhydrous acid; to this is added so much water that the flask is above one-fourth full, when 6·5 to 7 grms. neutral oxalate of potash (or 5·5 to 6 grms. oxalate of soda) are

conveyed into it; and lastly, 2·98 grms. manganese ore are weighed off in a glass tube, and in another tube the same quantity of pure pyrolusite, or of artificial hydrate of the peroxide of manganese. The tube containing the sample of manganese is suspended in A, the apparatus connected, counterpoised, the manganese made to fall into the sulphuric acid, and the operation effected as in the examination of acids. The loss in weight divided by 3 gives as above the per-centage of peroxide. The tube containing the pyrolusite is now conveyed into A, and the experiment repeated. If the first sample of manganese was pure pyrolusite, then it has wholly consumed the 5·47 grms. sulphuric acid (or 4·967 hydrochloric acid), and no further disengagement of carbonic acid can take place (and moreover the loss in weight will amount to nearly 3 grms.). But if any evolution of gas does result, the experiment is carried on to the end, and then the total loss in weight produced by the two samples is determined. Supposing that the manganese contained ingredients which have not combined with any of the acid, then the loss will be 3 grms.; but if it amounted to less, the centigrammes wanting will give, on being multiplied with 0·6114, the anhydrous sulphuric acid, or with 0·5552, the anhydrous hydrochloric acid, which have been uselessly consumed by foreign ingredients in the decomposition of 100 parts of the manganese under examination.

On a Substitute for White Lead in the Arts, which does not contain Lead. *By* M. DE RUOLZ.

The number of individuals attacked by saturnine diseases admitted during the last eight years to the *Hôpital de la Charité* has amounted to 1163; of this number 406 are workmen employed in the manufacture of white lead and 385 painters. The department of the Seine alone furnished in the year 1841, 302 patients, consisting of 69 painters and 233 white-lead makers. Of this number, 12 have died, and 1 is become insane. Of the 233 patients from the manufactories, 161 were from Clichi; and of the 12 who died, 7 were from this establishment, the only one which practises on a grand scale a peculiar process of manufacture. None of the expectations hitherto entertained respecting peculiar methods of manufacturing white lead have been justified by experience. The dangers then are inherent in the lead, and the only certain means of preserving a class of workmen who amount in Paris alone to near 8000, is to substitute a compound containing none of that metal.

We have experimented on a considerable number of white compounds, of which two only have combined the conditions of being useful, cheap, and not injurious to the health. One of these is oxide of antimony (flowers of antimony), which possesses the following qualities:—It has several advantages over white lead with the process of manufacture we have adopted; and being obtained direct from the native sulphuret of antimony, its adoption would impart a new stimulus in the working of the mines of antimony which abound in France. Its cost price is less than the third of that of white lead

of middling quality. It may be ground up with oil without any previous preparation, and the workmen would be exempt from all danger.—*Journ. de Pharm.*

PATENT.

Patent granted to William Henry Fox Talbot, Lacock Abbey, Wilts, *for Improvements in Photography.*

The first part of these improvements consists in removing the yellowish tint of pictures taken on calotype and other photographic paper, which has been prepared with a solution of nitrate of silver, by plunging the picture into a hot bath, composed of hyposulphite of soda (or any other soluble hyposulphite), dissolved in 10 times its weight of water, and heated to nearly the boiling point; the picture should remain in the bath about ten minutes, and be then washed in warm water and dried. By this means the picture is rendered more permanent and transparent, and its lights become whiter. After undergoing the above operation, the transparency of calotype pictures may be increased by causing melted wax to penetrate into the pores of the paper.

The second improvement consists in placing a warm plate of iron behind the paper-holder, during the process of taking a calotype picture with the camera, to communicate warmth to the prepared paper, and thus render it more sensitive.

The third improvement consists in preparing what the patentee terms io-gallic paper, by washing a sheet of iodized paper with a saturated solution of gallic acid in water, and then drying it. This paper will keep good for a considerable time if placed in a portfolio or press; and when wanted for use, it may be rendered sensitive to light by means of a solution of nitrate of silver.

The fourth improvement consists in washing iodized paper with a mixture of 26 parts of gallic acid, and 1 part, or thereabouts, of nitrate of silver (the solutions being of the strength usually employed in the calotype process); it can then be dried before a gentle fire without being spoiled. It is not quite so sensitive to light as the ordinary calotype paper; but it can be used in a dry state, whereas the calotype paper must generally be used in a moist state, as there is some difficulty in making it quite dry without more or less injuring it.

The fifth part of the invention relates to a method of improving the appearance of photographic pictures. A copy or reversed impression of a photographic picture is taken in the ordinary manner, except that it remains in the light twice the usual time; its shadows are thus rendered too black and its lights not sufficiently white. It is then washed and plunged into a bath of iodide of potassium (of the strength of 500 grs. to each pint of water) for one or two minutes, which makes the picture brighter, and its lights assume a pale yellow tint. After this it is washed, and immersed in a hot bath of

hyposulphite of soda, until the pale yellow tint is removed, and the lights remain quite white. The pictures, thus finished, have a pleasing and peculiar effect of light and shade, which is not easily attainable by other means.

The sixth improvement consists in waxing photographic pictures, to render them more transparent, and then placing a sheet of white or coloured paper behind them.

The seventh improvement consists in obtaining enlarged copies of Daguerreotype and calotype portraits, and other small photographic pictures, by throwing a magnified image thereof, by means of lenses, on a sheet of calotype paper, thus producing a magnified negative copy, from which positive copies can be obtained in the usual manner.

The eighth improvement relates to photographic printing. A few pages of letter-press are printed on one side only of a sheet of paper, which is waxed, if thought necessary, and the letters are cut out and sorted; then, in order to compose a new page, a sheet of white paper is ruled with straight lines, and the words are formed by cementing the separate letters in their proper order along the lines. The page being completed, a negative photographic copy is taken from it, having white letters on a black ground; this is fixed, and the required number of positive copies is then obtained. Another method is to employ larger letters, painted on rectangular pieces of wood, coloured white, and forming pages therewith, by arranging them in rows on a tablet or board suitably grooved for that purpose; a copy (of the size desired) is then taken on sensitive paper by a camera-obscura.

The last part of the invention relates to what the patentee terms photographic publication; that is, producing a number of positive photographic copies of a picture or print for the purposes of sale. The objects most suitable for such publication are prints, engravings, drawings, letter-press, maps, music, and similar productions. Copying paper is first prepared by taking good writing-paper, without water-mark, and dipping it in a salt-water bath, consisting of 3 or 4 ounces of salt to each gallon of water; it is then wiped and dried. After this it is washed in a solution, formed by mixing 100 grs. of nitrate of silver with 2 oz. of distilled water, then adding a sufficient quantity of ammonia to form a precipitate, and redissolving the same, leaving the solution clear. When dry the paper may be used for obtaining a negative copy of any print or picture, by placing it in contact therewith in a copying-frame (consisting essentially of a piece of glass, with a board at the back, and tightening screws), and exposing it to the light until the negative copy is produced. The negative copy is fixed by a hot solution of hyposulphite of soda, as before described, and may also be waxed; the requisite number of positive copies are then obtained from it, and are fixed in the manner above mentioned.—Sealed June 1, 1843.

THE CHEMICAL GAZETTE.

No. XXXI.—February 1, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Iodine on Tartar-Emetic. *By* W. Stein.

M. Preuss found that on allowing a cold solution of 34 grs. iodine and 100 grs. tartar-emetic in 2 oz. of water to stand for some time, a compound was deposited in the form of golden-yellow spangles, which on being exposed to heat was converted under evolution of iodine into oxide of antimony. The author has submitted this reaction to a closer examination; he found, in the first place, that the solution of tartar-emetic is in most cases rendered turbid on the addition of iodine, and deposits white oxide of antimony, which after a time is converted into the yellow precipitate. He could never obtain the combination in a crystalline state, except when a little free tartaric acid was added to the solution of tartar-emetic previous to the addition of the iodine. Frequently there is formed a second heavier compound, besides the yellow combination, which is of a brown-red colour. The *yellow* combination may also be obtained in the following manner:—1st. When an alcoholic solution of iodine is conveyed in excess into a concentrated solution of tartar-emetic, to which some free tartaric acid has been previously added: the solution of iodine is added by degrees, and continued until the liquid, after standing for a short time, is no longer decolorized. After some time the compound separates in golden spangles, but since it is soluble in free tartaric acid, there remains more or less in solution according to the quantity of tartaric acid previously added.

2nd. When 1 part iodine is triturated to a paste with 2 parts tartaric acid and a little cold water, there is no increase of temperature; the mass acquires a yellow colour, the water a brown one, and on applying heat the whole of the iodine is dissolved.

3rd. The chloride of antimony may be employed instead of tartar-emetic, but then iodide of sodium or iodide of potassium must be taken instead of free iodine, the liquid evaporated to dryness, again treated with water and evaporated, and this repeated several times, otherwise very little or none of the compound is obtained. In this manner however its formation is slow and difficult.

In colour and external appearance this compound, whether crystallized or not, resembles to deception iodide of lead. It is par-

tially decomposed by water, especially by hot water, which takes up a reddish-brown combination, that is also contained in the solution of tartar-emetic from which the yellow substance was deposited. It is readily and entirely dissolved by muriatic acid, imparting to the liquid a brownish colour. The solution contains free iodine, and affords on evaporation the same reddish-brown compound and chloride of antimony. On saturating the free acid with an alkali, the original combination is not re-obtained; there is only a precipitation of oxide of antimony. It dissolves entirely in tartaric acid and in tartrate of potash, but with far more difficulty than in muriatic acid. It is decomposed by nitric acid, with separation of oxide of antimony. It is apparently not attacked by very dilute sulphuric acid even with the application of heat; acid of 1·75 does not appear to act on it in the cold, but on being warmed the quantity of the substance decreases perceptibly, and that which remains behind has a brownish-red colour; the acid itself is not coloured, and contains oxide of antimony in solution. It is perfectly soluble in a solution of caustic potash and of sulphuret of ammonium. Carbonate of soda decomposes it, with separation of oxide of antimony.

The substance dried at 212° Fahr. contains no water chemically combined. Heated in a glass tube, it gives off a small quantity of free iodine, upon which a very volatile sublimate is deposited in the upper portion of the tube in drops, which are of a brownish-red colour, and on cooling solidify to a crystalline mass, when the colour becomes paler. Behind this is deposited a very slight yellowish film, apparently of the undecomposed compound, and at the bottom of the tube there remains fused oxide of antimony. An empyreumatic æthereal odour, distinct from that of burnt tartaric acid, is always perceptible at the commencement of the ignition. No disengagement of oxygen could be perceived, probably owing to this slight admixture of organic substance, although the action of hydrochloric acid proves that there must be a small quantity of iodic acid in the compound. Since it is partially decomposed by water, it must not be edulcorated too long, and only with cold water. It is indeed very difficult to obtain it perfectly pure.

The following course was adopted in the analysis:—The antimony was precipitated once with iron, but this method was not again followed in the other analyses. In all the other cases the solution of the substance in muriatic acid was freed from antimony by long-continued treatment with sulphuretted hydrogen gas, the sulphuret of antimony collected on a weighed filter, (dried at 212° Fahr. with the usual precautions) then dried at 212° Fahr. until it lost no more in weight, and lastly a weighed portion was oxidized in a long-necked flask with fuming nitric acid. The sulphuric acid was then precipitated with chloride of barium, and the usual course followed.

To determine the iodine, the compound was in every instance boiled for some time with carbonate of soda (which should be perfectly free from chlorine) and water, the liquid filtered from the oxide of antimony, and after this had been well washed some nitrate of silver, and then an excess of nitric acid added to the solution with

the necessary precaution. The iodide of silver was placed in the warmth to subside, the liquid separated by means of a pipette according to Liebig's method, the iodide of silver dried at 212° Fahr. and weighed.

The following are the results of several analyses :—

Sb	57·657	58·630	59·420	57·720	60·110
J.....	32·184	32·330	32·820	33·490	

The sublimed compound, analysed in the same manner, gave 24·8 per cent. of antimony. The formula Sb^2J^3 requires in 100 parts 24·5. This appears therefore to be the neutral compound and corresponding to the oxide. It sublimes in brown drops, which on cooling solidify to an apparently prismatic crystalline mass. It is decomposed by water, depositing the above-mentioned yellow combination, which is accordingly basic, as also appears from its behaviour in the glass tube. The composition of the yellow compound is now easily ascertained. If the neutral combination just described is combined in it with oxide of antimony, we have to calculate how much antimony the ascertained 32·706 per cent. iodine require to form Sb^2J^3. This amounts to 11·13, and there remain 47·577 of the 58·707 found, which exist therein in the state of an oxide, and form with 9·703 oxygen, 57·28 oxide. 100 parts therefore contain 43·836 Sb^2J^3 and 57·280 Sb^2O^3.

Calculated in atoms it agrees best with the formula $Sb^2J^3 + 5Sb^2O^3$, which in 100 parts requires 60·00 Sb^2O^3.

The above five analyses would agree perfectly with this formula according to the above calculation; on the other hand, the smallest quantity of antimony found, and the largest quantity of iodine, lead to the formula $Sb^2J^3 + 4Sb^2O^3$, which requires in 100 parts, 54·5 Sb^2O^3.

I may make a few observations respecting the brownish-red body which is frequently found along with the above-mentioned basic compound. Its remarkable specific gravity has already been noticed; this is so high that it is difficult to remove it with water from the glass, from its subsiding so rapidly.

It is crystalline, of brownish-red colour similar to officinal kermes, and undergoes no perceptible change from contact with water. I had too little of it at my disposal to ascertain its other properties. It afforded on analysis 21·38 per cent. antimony.

The liquid from which the basic compound has been precipitated is of a brown colour, has a very acid reaction, and leaves on evaporation a black lustrous residue, frequently metallic (resembling iron pyrites), which however dissolves in water to a colourless solution, frequently leaving behind a large quantity of basic iodide of antimony. When this solution is mixed with alcohol, a white salt is precipitated, which contains no iodine, but only potash and antimony. It contains 13·17 per cent. potash, just as tartar-emetic.

To find out the proportion of oxide of antimony and potash in the liquid not treated with alcohol, so as to be able to draw some conclusion respecting the degree of change which tartar-emetic undergoes from the action of iodine, the iodine was precipitated from

one portion by silver, and after the separation of the silver by muriatic acid, the antimony was thrown down by sulphuretted hydrogen, the potash determined as above by evaporation and ignition of the residue; when it became evident that 0·2713 potash was contained in it for every 0·4173 oxide of antimony, which approaches very nearly to the proportion of 2 atoms potash to 1 atom oxide of antimony.

Besides oxide of antimony and potash with tartaric acid, the presence of iodide of potassium may also be demonstrated in the liquid, for when this is evaporated to dryness, and the ignited residue extracted with alcohol, iodide of potassium is dissolved out. The quantity of potassium combined with iodine contained in the same liquid, which had served for the determination of the potash and oxide of antimony, was ascertained by the determination of the iodide. 1·432 iodide of silver was obtained, which correspond to 0·288 potash; this amounts to nearly the half, supposing the liquid also to contain an excess of iodine. Of every 2 atoms of potash there is 1 atom in combination with iodine.

The liquid contains no more tartar-emetic, for none crystallizes from it, and iodine causes no further precipitate in it; when, on the other hand, alcohol is added to it, it deposits a salt which has the composition of tartar-emetic. This seems to prove that the compound dissolved in the liquid is the so-called neutral tartar-emetic described by Knapp.

Knapp mentions, it is true, that this is decomposed by alcohol into tartaric acid and ordinary tartar-emetic, of which it may also be composed. This was not observed with the liquid in question; on the contrary, the alcoholic liquid still contained antimony and potash, which did not solely arise from the iodide of potassium, but amounted to more; the amount of potash, however, viz. 9·27 per cent., in the residue of evaporation of this liquid, appears to speak in favour of the identity of the two compounds.

The above-mentioned behaviour of tartar-emetic to iodine, the separation which takes place of only half of the antimony in the state of iodide, the formation of iodide of potassium, and in general the separation of oxide from tartar-emetic, both by acids and by alkalies, may be very readily explained by supposing the half of the oxide of antimony to exist in tartar-emetic in the state of oxide of antimony-potash, and by constructing the formula for tartar-emetic as follows:—$Ko, Sb^2 O^3, \overline{T}^2 + Ko, Sb^2 O^3$. Iodine first decomposes the oxide of antimony-potash, forming iodide of potassium and iodate of potash, and oxide of antimony is eliminated. When there is an excess of iodine, and only then, the decomposition proceeds further, and neutral iodide of antimony is formed. The elimination of water from tartar-emetic at high temperatures has nothing to do with its constitution.—*Journ. für Prakt. Chem.*, xxx. pp. 48–61.

Analysis of the Blood in a Case of Lead Colic. *By* Prof. Cozzi.

This blood was taken from a patient suffering under lead colic. Prof. Cozzi detected in it a salt and an oxide of lead; and he further remarked, that instead of being mixed with the hæmatosine, the globuline or fibrine, it was combined with the albumen.—*Gazette des Hôpitaux* for Jan. 1844.

On the Constitution of the Succinates. *By* M. Döpping.

[Continued from p. 33.]

Neutral Succinate of Magnesia.—$MgO\,\overline{S} + 6$ Aq. Succinate of soda produces no precipitate even in very concentrated solutions of salts of magnesia. Carbonate of magnesia dissolves readily in a hot solution of succinic acid, and on evaporating the neutral solution at a gentle heat, the salt separates slowly in prismatic crystals. It is not changed by exposure to the atmosphere, is neutral, easily soluble in water and insoluble in alcohol. Ammonia precipitates from the solution a basic salt, which is insoluble in water. The dry salt does not lose the whole of its water at 212°, a small quantity remains behind at 266°, but the portion which escapes above 212° does not amount to an equivalent. The salt lost no more water when heated to 392°, and afforded 43·2 Aq and 16·35 magnesia; the formula requires 43·27 and 16·53.

Basic Succinate of Magnesia.—$(MgO)^3\,\overline{S}$. The precipitate caused by ammonia in a neutral solution of succinate of magnesia is in the form of a white powder, which is insoluble in water, alcohol and acetic acid; heated to 392°, it gives off 10·83 per cent. water and 49·24 magnesia; the formula requires 10·73 and 49·30.

Succinate of Magnesia and Potash.—$MgO\,\overline{S} + KO\,\overline{S} + 5$ Aq. The author obtained this salt by neutralizing a weighed quantity of succinic acid, dissolved in water, with carbonate of magnesia, then adding the same amount of acid, and neutralizing this with carbonate of potash; on evaporation, first at a gentle heat, and subsequently by exposure to the air, the salt crystallized in very regular hexagonal double pyramids. It is easily soluble in water, with some difficulty in weak alcohol, is not changed by exposure to the air, and has no action upon vegetable colours. The salt from which the water of crystallization has been expelled by heat, absorbs moisture when exposed to the atmosphere, and deliquesces. Heated to 392°, it loses 20·77 water, and contains 9·72 magnesia and 22·2 potash; the formula requires 21·08 Aq, 9·68 MgO, and 22·12 KO; the salt however does not appear to be produced under all circumstances.

Succinate of Nickel.—$NiO + 4$ Aq. Recently-precipitated hydrated oxide of nickel dissolves readily in a hot solution of succinic acid; the solution is pale green on evaporation under the bell-glass; over sulphuric acid the salt separates in small verrucous-green indistinct crystals, which are free from succinic acid, and when brought on to moist litmus-paper do not alter it; they are insoluble in

alcohol, soluble in water, acetic acid and ammonia. To remove any adherent succinic acid, the salt was reduced to a powder and washed with alcohol. At 212° it lost the whole of its water, with the exception of a small portion which was not completely expelled at 266°, but was far less than an equivalent. The salt contains 29·08 water and 30·38 oxide of nickel; calculation requires 29·07 Aq, 30·34 NiO.

Succinate of the Protoxide of Manganese.—$MnO\,\bar{S} + 4$ Aq. Protocarbonate of manganese is readily dissolved by a hot solution of succinic acid, carbonic acid being evolved. On slow evaporation well-developed shining amethyst-red prisms separate from the faintly-coloured liquid. The salt is insoluble in alcohol, soluble in water; it is neutral, and is not changed by exposure to the air. The salt gives off the whole of its water at 212°, so that a very inconsiderable loss in weight results upon heating it subsequently to 392°. It contains 28·71 water and 29·57 protoxide of manganese; the formula requires 28·92 Aq and 29·26 MnO.

Succinate of Zinc.—$ZnO\,\bar{S}$. When freshly-precipitated carbonate of zinc is conveyed into a boiling solution of succinic acid very slowly and in small quantities, a white crystalline powder separates, which is of difficult solution in water and in succinic acid, is insoluble in alcohol, easily soluble in dilute mineral acids, acetic acid, potash and ammonia; it has no action on moist litmus-paper; the salt loses but very little hygroscopic water when heated to 212°, nor is there any further decrease in weight when heated to 392°. It contains 44·67 ZnO (theoretical 44·78).

Succinate of Copper.—$CuO\,\bar{S}$ is prepared in the same manner as the succinate of zinc. The solution of a copper salt is not thrown down by succinate of potash or soda. The salt forms a bluish-green crystalline powder, which dissolves with difficulty in water and in a solution of succinic acid, more readily in acetic acid; it is insoluble in alcohol. It contains no water of crystallization, but 44·11 CuO (theoretical 44·10).

Succinic Acid and Oxide of Chromium.—The solution of a salt of oxide of chrome is not altered by that of an alkaline succinate. Freshly-precipitated hydrated oxide of chrome dissolves but in very small quantity in a hot solution of succinic acid; on evaporation the acid separates in green crystals, owing to a minute quantity of oxide of chrome, without however having entered into chemical combination with it.

Sesquibasic Succinate of the Peroxide of Iron.—$Fe^2\,O^3\,\bar{S}^2$. When succinate of soda is added to a solution of neutral perchloride of iron, a gelatinous voluminous precipitate of reddish or cinnamon-brown colour separates slowly from the liquid; it is difficult to filter and to edulcorate with water, from its agglomerating to a firm doughy mass. Nor is it much easier to wash in the vessel in which the precipitation was effected. This precipitate is insoluble in cold water and in alcohol; boiling water dissolves a small portion; cold acetic acid dissolves it with difficulty, but very readily when warmed;

it is easily soluble in dilute mineral acids. When dry it forms dark reddish-brown pieces, which are easily reduced to a dark tile-red powder. It is very tenacious of moisture, from which it can only be freed entirely at 356°; it is also very hygroscopic. Dried at 392°, it contains 43·47 $Fe^2 O^3$ (theoretical 43·78).

This combination is the same as that obtained in analytical researches, when iron is separated from manganese by an alkaline succinate, which has been almost generally regarded as a neutral salt, and has been asserted to be decomposed by boiling water into a basic and into an acid salt, on which account the use of cold water is recommended for edulcorating the above precipitate in quantitative determinations. It is evident that when the above compound is formed on mixing an alkaline succinate with perchloride of iron, and the whole of the alkali is in combination with acid, there must be an equivalent of free acid in the liquid in which the salts were dissolved. It is owing to this, that on washing with hot water, a small portion of the precipitate is carried through the filter. But the quantity was found to be very small compared with the residue remaining on the filter, and on evaporating the solution in the water-bath, a dark reddish-brown mass was obtained, of which 0·437 washed with alcohol and dried at 392°, gave on ignition 1·92 peroxide of iron. In the alcohol with which the salt was edulcorated free succinic acid could be detected.

When the gelatinous precipitate of succinate of iron is conveyed into a boiling hot solution of succinic acid, and left for some time in contact with it, being frequently shaken, a large quantity of the precipitate is dissolved; but on evaporating the solution to crystallization, even over the water-bath, the greater portion of the dissolved salt frequently separates in flakes, and on crystallization succinic acid coloured by some succinate of iron alone is obtained, from which it may easily be separated by means of alcohol. This is Wenzel's acid succinate salt of iron which crystallizes in laminæ.

When a solution of perchloride of iron is mixed with one of acetate of soda, and succinate of soda added to it, a pale tile-red precipitate is obtained, which is not gelatinous, soon subsides, and may be readily filtered. On edulcorating it with water, it assumes the gelatinous transparent condition of the one above described, without however its chemical composition being in any way altered; if, on the contrary, the precipitate is washed with alcohol of ·898 sp. gr., its physical consistence is not altered, it remains pulverulent, subsides easily, and allows of the liquid passing through the filter without any difficulty. It was found to have exactly the same composition as the one previously described.

Succinate of Iron with 27 Atoms of Base?—$(Fe^2 O^3)^9 \bar{S}$. On adding an excess of ammonia to the freshly-precipitated gelatinous sesquibasic succinate of iron, it loses for the greater part its gelatinous consistence, the colour becomes darker, and on filtering the liquid, washing and drying the residue, a blackish-brown friable mass is obtained, which on being heated to 392° leaves on ignition 93·2 per cent. On calculating from this the atomic weight of the

salt the number 1049·89 is obtained; after deduction of the oxide of iron there remains 71·46, which nearly corresponds to the one-ninth of an equivalent of succinic acid.

When the freshly-precipitated sesquibasic succinate of iron is treated with hot solution of ammonia, it is deprived of still more succinic acid, but by no means of the entire amount. Whether these two latter combinations of succinic acid with iron are in constant proportions, the author does not venture to assert.

Succinate of Silver.—$AgO\,\overline{S}$. Free succinic acid causes no precipitate in a solution of nitrate of silver, but with succinate of soda there is produced immediately a white pulverulent non-crystalline precipitate, which soon subsides and is very easily edulcorated; it is insoluble in alcohol, very difficult of solution in water and in acetic acid, but dissolves readily in ammonia and dilute nitric acid; it loses but very little in weight at 212°; at 302° it begins to change its colour, becoming greenish-gray, which grows darker in proportion as the temperature is raised. It contains 69·91 AgO (theoretical 69·79).

Neutral Succinate of Lead.—$PbO\,\overline{S}$. On adding a solution of succinic acid to one of sugar of lead, neutral succinate of lead separates as a white powder. The same precipitate is obtained on mixing a lead salt dissolved in water with a solution of alkaline succinate, or on mixing basic acetate of lead with aqueous succinic acid. When it is precipitated from hot liquids it is generally crystalline; the neutral salt dissolves but very sparingly in water and acetic acid, easily in dilute nitric acid and solution of potash, is converted by ammonia into a basic salt, and is insoluble in alcohol. Dried at 212°, the crystalline salt loses scarcely a few per cent.; the loss does not increase when heated to 446°; above this temperature it begins to lose its white colour. It contains 69·12 PbO (theoretical 68·94).

Sesquibasic Succinate of Lead.—$(PbO)^3\,\overline{S}$. On adding, as above mentioned, a solution of succinic acid to basic acetate of lead, a crystalline precipitate is formed when it is thrown down from hot solutions, which has exactly the same composition as the neutral succinate of lead; but it is quite different when a solution of bisuccinate of soda is added to basic acetate of lead. If the two solutions are mixed warm, a plaster-like precipitate is formed, which deposits itself on the bottom and sides of the vessel, is tenacious in warm water like a plaster, and becomes hard and brittle in the cold. Exposed for some time to contact with the atmosphere, the mass may be broken to pieces and dried at 212° without aggregating; in this state it is easily reduced to a powder. Ammonia deprives the powdered salt, with the assistance of heat, of acid, and converts it into a still more basic combination. It is dissolved by potash; acetic acid deprives it of some oxide of lead, converting it into neutral salt. Water and alcohol dissolve none of it. When the salt, dried at 266°, is heated for some time in the oil-bath to 440°, some water escapes, it loses its white colour and gradually becomes darker. The salt dried at 266° contains 76·97 PbO (theoretical 76·90).

Tribasic Succinate of Lead.—$(PbO)^3\,\overline{S}$. When the neutral salt is treated with an excess of solution of ammonia, it is deprived of some succinic acid, and there remains a white powder, which is easily soluble in potash and dilute nitric acid, but insoluble in water and in alcohol; on being warmed with acetic acid, it is deprived of some oxide of lead and converted into neutral succinate of lead. The salt loses very little water at 212°, and there is no further decrease in weight up to 392°. It contains 86·88 PbO (theoretical 86·94).

Succinic Acid and Protoxide of Mercury.—On mixing a solution of the protonitrate of mercury with one of succinate of soda, a white heavy precipitate is obtained, which does not dissolve in an excess of succinic acid, is insoluble in water and alcohol, but is readily dissolved by dilute nitric acid. It was found on analysis to be a mixture of basic protonitrate of mercury and succinate of the protoxide of mercury.

Succinic Acid and Peroxide of Mercury.—Succinic acid produces no change in a solution of perchloride of mercury. Recently-precipitated hydrate of the peroxide of mercury is converted, by long-continued boiling with a solution of succinic acid, partly into a white powder, which according to analysis contains more oxide than corresponds to an equivalent of succinic acid to form a neutral salt; a small quantity of the mercury remains dissolved in the liquid. On conveying succinate of soda into a solution of corrosive sublimate, no precipitate is obtained, even on the evaporation of a portion of the liquid; but on allowing the solution to stand, there separates, if it be sufficiently concentrated, a salt in fine silky needles, which contains chlorine, succinic acid, peroxide of mercury and soda, and is probably a double salt of perchloride of mercury and succinate of soda. If peroxide of mercury be dissolved in acetic acid at a gentle heat, and succinic acid conveyed into the solution, then evaporated at a gentle heat to dryness, in order to expel the acetic acid, and the residue extracted with alcohol to remove any excess of succinic acid, a white powder remains, which dissolves with great difficulty in water, is free from acetic acid, and on being treated with muriatic acid affords a white powder, consisting of protochloride of mercury.

Succinic Acid and Oxide of Antimony.—Succinic acid does not appear to form any combination in definite proportions with oxide of antimony. A solution of tartar-emetic is not changed either by succinic acid or by succinate of soda: the latter throws down from protochloride of antimony a basic salt which contains chlorine. The author did not find Berzelius's statement of oxide of antimony being soluble in succinic acid confirmed, for freshly-precipitated oxide of antimony was dissolved in very small quantity, either by a solution of succinic acid or by the bisuccinate of potash, with or without the assistance of heat.—*Ann. der Chem. und Pharm.*, xlvii. pp. 253–291.

Proposed Nomenclature for the Acids of Sulphur.

Berzelius, in the new edition of his 'Manual,' separates the acids of sulphur into monothionic acids (sulphuric and sulphurous acids), dithionic acids (dithionic or hyposulphuric acid, and dithionous or hyposulphurous acid), trithionic acid (Langlois' sulphated hyposulphuric acid), and tetrathionic acid, for the bisulphated hyposulphuric acid of Fordos and Gélis. In future we shall employ these names for the two new acids.

On the Influence of Oxygen in reddening the Blood. *By* Prof. Nasse.

The following is a series of deductions made from experiments previously detailed by Prof. Nasse (in Wagner's 'Handwörterbuch der Physiologie'), respecting the relative influence of oxygen gas and saline matters in reddening the blood.

1. Oxygen gas has the power of reddening the blood without the presence of salts.

2. When the carbonic acid gas contained in blood is separated (as far as possible), and oxygen gas is not added, and the normal quantity of salts not interfered with, the blood does not become reddened.

3. The alkaline salts indeed redden the blood, when added to it in considerable quantity, without the presence of oxygen, but they by no means impart to it the peculiar colour of arterial blood.

4. The alkaline salts, when their quantity is increased, hasten and render more intense the reddening of the blood by oxygen.

5. Under these two conditions they redden the blood, both when the oxygen gas is mixed with much carbonic acid, and when the blood is strongly impregnated with the latter.

6. Also without increase of the saline contents, the blood impregnated with carbonic acid is gradually reddened by oxygen gas, and indeed without much of the former being removed.

7. The spontaneous change of the florid red into dark blood (through the development of carbonic acid gas) is hastened by a certain addition of alkaline salts (but not carbonates).

8. Moreover this addition limits the absorption of both the carbonic and oxygen gases, whilst the latter is changed into carbonic acid in smaller quantity than usual.

9. At the same time it diminishes the removal of the carbonic acid from the blood by oxygen.

10. The alkaline carbonates, on the other hand, as well as pure ammonia, promote the removal of the carbonic acid gas, and retard the spontaneous alteration of the colour of the fluid blood.

Analysis of a Liquid taken from Vesicles on the Skin of the Umbilical Region. *By* M. Girardin.

This fluid was alkaline; it did not coagulate spontaneously; it frothed strongly by agitation. When heated it was coagulated in

the same manner as the serum of the blood, and gave off the odour peculiar to boiled albumen. It was miscible with water; alcohol rendered it milky, and precipitated white flocculi. Acids, tincture of galls and metallic solutions acted upon it as upon the serum of the blood. When evaporated at a low temperature it did not become turbid, but was at last reduced into thin yellowish transparent plates, just as is the case with white of egg. The coagulum formed by heat swelled in alkalies without dissolving. It was slowly dissolved by cold concentrated muriatic acid, developing a bluish-green colour. These characters all indicated that the fluid of the vesicles had much analogy with the serum, and that it was entirely formed of albumen. When carefully analysed it gave the following composition:—

Water	93·9500
Albumen	4·9200
Cholesterine	·6475
Extractive, soluble in alcohol, with traces of free soda and common salt	·1075
Common salt, phosphate of soda and phosphate of lime	·3750
	100·0000

It thus differs notably from the serum by its richness in cholesterine, and more nearly resembles the serum of the blood from which the fibrine has been separated by coagulation than any other liquid. —*Journ. de Pharm.* for Jan. 1844.

ANALYTICAL CHEMISTRY.

On the Solubility of Bismuth, Sulphuret of Antimony and Sulphuret of Arsenic in Hydrogen Gas. By Dr. Meurer.

The author found, while experimenting on Marsh's test, that bismuth was dissolved in hydrogen, and that the gas so obtained, on being ignited, left a stain on the plate of porcelain which differed externally from the film of arsenic, and on further examination was not at all liable to be confounded with it. The hydrogen gas dissolves but little of it, and it is only formed on the energetic decomposition of water, or of muriatic acid by zinc when some perchloride of bismuth has been added to the mixture. The flame is not so white as with arseniuretted hydrogen; the stain is but small, and forms more in the centre of the flame; it is of a very pale gray, exhibits no play of colours, and does not dissolve in Labaraque's liquid. In mixed films, consisting of bismuth and arsenic, the outer margin was dissolved by the bleaching liquid, but the central point of bismuth was left untouched. This probably accounts for some persons having asserted that pure *magisterium bismuthi* contains arsenic, while others have maintained, on the contrary, that arsenic is never present in this preparation, because the stain produced has

quite a different appearance. The bismuth is not mechanically carried over, for the author obtained it even when a tube containing asbestus was interposed. The determination is rendered difficult from the circumstance, that when the bismuth is mixed with arsenic films are obtained, sometimes of pure arsenic, sometimes of bismuth, and sometimes the two mixed, which renders it necessary to examine all the films. This is avoided when the metals to be separated are collected in a glass tube. To examine bismuth it must be previously converted into basic nitrate; it is then dissolved in muriatic acid, and this solution conveyed into the apparatus from which the gases are generated. Dr. Meurer moreover found that not only simple but also compound bodies dissolved in hydrogen gas, for instance sulphuret of arsenic and sulphuret of antimony. This observation appeared to be of importance, as affording a means of distinguishing between the two, and it may be employed for this purpose; but there are now many better methods of distinguishing arsenic from antimony; it is however a fact of more general interest, first, because it was hitherto not known that these sulphurets were soluble in hydrogen gas, and might be again separated by combustion of the hydrogen; and secondly, because it shows that sulphuretted hydrogen may sometimes occur contaminated with sulphuret of arsenic and sulphuret of antimony.

To obtain these combinations, it is best to add some *aqua hydrosulphurata* to the liquid containing arsenic or antimony to be examined, which is then conveyed into the apparatus in which the hydrogen gas is generated; this is more advantageous than evolving sulphuretted hydrogen from sulphuret of iron, for the formation then results unequally, and at the beginning films of arsenic and antimony are obtained, and only subsequently those of sulphuret of arsenic and sulphuret of antimony. They are easily distinguished from the mere sulphur stain produced on burning sulphuretted hydrogen, for this is always very inconsiderable, and does not dissolve in solution of caustic ammonia. Arsenic and antimony differ by their colour, which is less apparent in the mixed films.—*Archiv der Pharm.*, for October 1843.

PHARMACOLOGY.

On Radix Sumbul, *the Persian Musk Root**. *By* H. Reinsch and M. Buchner.

Notwithstanding the great intercourse with Persia, this interesting root appears to be as yet entirely unknown in Europe; the only notice of it is given by Erdmann and Ledebour in Dierbach's edition of the botanical portion of Geiger's 'Pharmacy.' It is there stated to be imported from Bokhara into Russia, and is said to resemble the white Hellebore, and to have a blackish-gray epidermis (which does not agree with the roots now under consideration), and

* A short notice of this root appeared at p. 657 of the first volume of this Journal.—Ed.]

to contain much mucus and an acrid resin having the odour of musk, but no essential oil, although the water distilled from it possesses a smell of musk. This root is not mentioned in any other pharmacological work, and even the 'Pharmacopœia Persica,' which appeared in Paris in 1681, contains no reference to it. It may now be had in Nuremburg and Hamburg at a very cheap rate. According to information supplied us by one of the importers, it comes from Persia by way of Nischnei-Novogorod to Europe, and is employed in Persia, on account of its odour, against mephitic vapours.

The root is very thick, fleshy, tuberose, and cut into discs of the diameter of from 1 to 4 inches, and in height from $\frac{1}{2}$ to $1\frac{1}{2}$ inch. From the pieces of the upper part of the root, it is evident that the stem can scarcely be 1 inch in thickness. The root divides downwards into a few thick branches, and appears to have very few lateral fibres; the epidermis is thin, grayish-brown, somewhat wrinkled, *i. e.* provided with diagonal furrows or corrugations; the parenchyma appears in the fresh state to be very fleshy, but dried it is cellular, foliaceous, and containing very numerous globules of starch; the freshly divided surface is yellowish-white, and is rendered dark blue by iodine, but as the root occurs in commerce the surfaces appear of a dirty brownish-yellow colour, and partly covered with exuded and dried milk-sap. The taste is spicy, bitter, of considerable duration, but not disagreeable; but the most peculiar character is undoubtedly its odour, which at some distance rebles musk so strongly and distinctly, that several pharmaceutists, whom we asked to smell the paper in which a slice of the Sumbul root was folded in order to have their opinion, unanimously pronounced it to be musk; but when held near, and especially with a fresh section, the odour resembles at the same time that of Apium, or somewhat that of Angelica. The odour adheres very strongly to linen, and is not entirely removed by washing; the taste is slightly sweet, musk-like, subsequently aromatic. Since the odour of musk is increased by ammonia, the authors placed some fine sections of the root in a glass, and moistened them with very dilute solution of ammonia, but now another aromatic odour appeared instead of the musky one. Dilute sulphuric acid also produced a different odour, which might almost be termed a rotten one; but on dropping a little *concentrated* sulphuric acid on a slice of the root, a very strong and decided odour of valerianic acid was produced, and the liquid became of a beautiful wine-red colour, which after a few hours passed into brown, while the smell of the acid still continued.

Reinsch submitted the root to analysis, and obtained the following result:—

Water	0·130
Essential oil, not smelling of musk	

1. *Extract with Æther.*

A nearly-colourless balsam	0·126
A waxy substance	0·002

2. *Extract with Alcohol of* 0·8194 *spec. grav.*

Balsam	0·002
Aromatic resin	0·003
A bitter substance, soluble in alcohol and water	0·010

3. *Extract with Alcohol of* 0·9335 *spec. grav.*

Bitter substance, soluble in water with vegetable gelatine and vegetable acid salts	0·064
A bitter yellow colouring substance, soluble in alcohol	0·040

4. *Extract with Water.*

Gum, soluble in cold water	0·082
Starch and salts	0·284
Gelatinous sediment	0·072

5. *Extract with Solution of Potash.*

Starch (in combination with the fibre)	0·100
Insoluble fibre	0·076
	0·991
Loss	0·009

The most interesting substance in this root is the balsam which æther extracts, which resembles in consistence and colour copaiva balsam. It possesses a burning aromatic taste, but only a faint musky odour, which however is strongly developed when the balsam has been placed for some time in contact with water; it differs very decidedly in its properties from most other vegetable substances; for instance, it dissolves in sulphuric acid with a splendid blue colour. This reaction is best obtained when a concentrated alcoholic solution of the balsam is dropped into sulphuric acid diluted with its equal weight of alcohol.

When the balsam is heated alone in the retort, a clear yellow oil, having a taste of peppermint, distils over at the commencement, after which the residue in the retort is converted into an indigo-blue mass, and finally an emerald-green oil passes over.

The balsam is easily soluble in solution of potash, and forms with it a crystalline mass; when this is dissolved in water and decomposed with sulphuric acid, the balsam is re-obtained apparently unaltered; but if some water is poured over this, and it is then placed aside for a few days, it becomes partially converted into beautiful transparent prisms, which have a most powerful odour of musk. Some other constituents of this root likewise appear to be extremely interesting in a chemical point of view.

The root therefore is in every respect similar to Angelica, and is certainly derived from some large umbelliferous plant; but it is of a brighter colour, with fewer ramifications or fibres, less spicy in taste and more bitter, and has a totally distinct odour. It might perhaps be supposed that the odour had been artificially communicated, perhaps by packing it between empty musk-pods; and this suspicion might receive additional support from musk being consumed by the Persians in considerable quantity, not only as an article

of luxury, but also as medicine, for we find in the Persian Pharmacopœia a considerable number of compound medicines of which musk forms a constituent. The authors however are not inclined to this opinion, because the odour is not merely externally adherent, but is also disengaged from fresh sections of the root. Undoubtedly it is closely allied to Angelica in its medical properties.—Buch. *Rep.*, xxxii. p. 210.

On Madder. *By* M. Girardin, Professor of Practical Chemistry at the Municipal School of Rouen.

[Continued from p. 48.]

5. On the Adulteration of Madders and Methods of detecting them.

On account of the high price of madder, and especially from the facility of introducing into this substance, which is sold in the form of powder, foreign pulverulent matters, which the most practised eye cannot detect, this root is subject to a number of sophistications which cannot be too fully exposed.

There are two kinds of adulteration. Sometimes earthy or mineral substances are incorporated with the powder of madder; sometimes vegetable substances are added to it, the colour of which resembles that of madder.

1. *Adulteration by Mineral Substances.*—The mineral substances which have been introduced, or which are still found in ground madders, are brick-dust, red and yellow ochre, yellowish sand, yellowish clay or argillaceous earth. A madder which contains earthy substances grates between the teeth when chewed.

A small quantity of such a madder, for example from 25 to 30 grms., introduced into a large glass globe and diluted with 5 or 6 litres of water, quickly deposits the greater portion of the earthy substances at the bottom of the vessel. When the suspended madder is decanted and the deposit agitated with a fresh quantity of water, the earthy substances are isolated and may be examined.

However, to determine the proportion, more exact processes must be had recourse to. The best is that of calcining, at a red heat, in a platinum crucible.

5 grms. of the madder under examination are first dried completely at 212° Fahr., and are weighed with great exactness, and then put into the platinum crucible, which must be weighed beforehand. The crucible is shut and heat gradually applied. When perfectly incinerated, the crucible is taken out of the furnace, and left to cool and then weighed. Its weight being deducted from the quantity employed, the difference gives the proportion of cinders obtained.

These cinders are composed,—1st, of the fixed mineral matters contained in the root; and 2nd, of the earthy substances, foreign to the chemical constitution of the root, and which have been accidentally or fraudulently mixed with the madder.

Some experiments which I made with M. Labillardière on a large

scale, in 1828, showed us that madder which is very pure, and quite free from its epidermis, or any foreign earthy matter, and dried with care, gives by incineration 5 per cent. of ash; that the Lizaris of Provence, stripped of its pellicle, gives on an average 8·80 per cent. ash.

According to M. Henri Schlumberger, 100 parts of Alsatian Lizaris, washed in distilled water, and dried at 212°, give 7·20 per cent. of ash; whilst 100 parts of Lizaris of Avignon, prepared in the same way, give 8·766.

According to M. Chevreul, 100 parts of Lizaris from the Levant, dried at 212°, give 9·80 ash.

When an Avignon madder, SFF (the mark most generally used), subjected to the test of incineration, gives a greater weight of ash than 5 per cent., which I have taken as the mean of numerous experiments, the excess must be attributed to the presence of foreign earthy or sandy matters, either arising from adulteration or a careless preparation of the powder.

When the excess is only from three to four-hundredths, it is probably owing to some fault in the preparation of the madder, the manufacturer not having separated the epidermis (which is always coated with the earth which surrounds the root) carefully enough by grinding; but when the excess is above 4 or 5 per cent. or more, it is the result of fraud.

The madders obtained from the merchants give very variable results with respect to the proportion of ash which they furnish, as the following table shows:—

	Per cent. of Ash.
On 6 trials the mulle madder of Avignon gave	4·00
On 7 trials the madder SF of Avignon gave from ..	12·40 to 20·00
On 18 trials the madder SFF of Avignon gave from	7·40 to 23·00
On 4 trials the madder SFFRP of Avignon gave from	12·00 to 16·00
On 3 trials the madder SFFP of Avignon gave from	10·00 to 10·80
On 7 trials the madder EXTF of Avignon gave....	10·00

When in testing a madder by incineration, the quantity operated on amounts to 5 grammes, the weight of the ash must be multiplied by 20 in order to bring it to 100 parts, and from the figure obtained 7 parts, representing the mean weight of ash p. c. furnished by good madder subtracted; the surplus then represents the proportion of earthy matters or of sand added by the manufacturer. Consequently a madder furnishing 16·40 per cent. of ash will contain 9·40 per cent. of foreign matter.

[We are compelled from press of matter to postpone the conclusion of this article to our next number.]

On Opium.

M. Texier states that the differences which are found in the qualities of the various opiums from the same soil, are not solely owing to the composition of the collected juice of the poppy, but rather to the different states of the atmosphere during its collection.

It is well known that the opium is collected by forming some horizontal incisions round the capsules, and allowing the juice to flow slowly from it for twenty-four hours. If during this operation any rain, fog or moisture should occur, the quality of the opium suffers; a few hours' rain suffices entirely to destroy the opium harvest. For this reason the poppy is cultivated in Asia Minor, only on the large table-lands of Cappadocia and of Phrygia, in the neighbourhood of the town of Karahissar; it is not an excessively hot country that is favourable to the cultivation of opium, but it is requisite to be nearly certain that there should be no rain from the flowering season of the poppy until the opium is collected. The poppies are cultivated in Asia Minor on irrigated lands.

One of the causes of the bad quality of the opium collected in Asia Minor of late years, is the sophistication with Armenian bolus, and other earths to which it is submitted.—*Comptes Rendus*, Nov. 30, 1843.

CHEMICAL PREPARATIONS.

Process for obtaining Oxide of Zinc by Precipitation.
By M. E. Defferre.

When oxide of zinc is prepared in the dry way, it is necessary to use certain precautions in order to obtain it pure. It frequently happens that the first portions of oxide are coloured reddish-yellow by the presence of iron which exists in commercial zinc, and sometimes also by oxide of cadmium; it moreover frequently contains metallic particles, and is then dense and of a whitish-gray. The Codex of 1818 contained a process by precipitation, which consisted in decomposing the pure sulphate of zinc by the subcarbonate of potash, and subsequently decomposing the carbonate of zinc by calcination in a crucible. M. Soubeiran, in his excellent 'Traité de Pharmacie,' gives this process, mentioning at the same time that published by Wackenroder for obtaining a pure sulphate. The method we practise is very cheap and easy of execution. Take

Laminated zinc	125 grammes.
Hydrochloric acid	500 ...
Nitric acid	8 ...
Carbonate of lime	8 ...

The zinc is dissolved in the hydrochloric acid with the aid of a gentle heat, the nitric acid added to peroxidize the iron always present in commercial zinc, and the solution evaporated to dryness; it is then redissolved in water and the carbonate of lime added, allowed to stand twenty-four hours and filtered; the solution, being perfectly clear, is thrown down with a sufficient quantity of solution of ammonia added by degrees till there is no further precipitate; this is now carefully washed and dried in a moderately-heated chamber.

This process, which is shorter and less expensive than any of

those with which we are acquainted, always affords a beautiful product. The oxide obtained by this method is perfectly white, very light, insipid, inodorous, wholly soluble in acids, imparting no colour to them, and also entirely soluble in alkalies. We recommend that the ammonia be added by degrees until there is no further precipitate, this being soluble in an excess of alkali; if too much has been added, it suffices to heat the solution in order to volatilize the excess, when the dissolved oxide is again precipitated.

[The following observations on the above process are by M. Soubeiran.]

M. Defferre's method has now been published some time, but we wished to repeat it before giving it to our readers. The precipitation of the sulphate of zinc is well effected both by M. Wackenroder's process of purification or by that of M. Defferre. The precipitation by ammonia is certainly advantageous; very little oxide of zinc remains in solution, and the precipitate, after being well edulcorated, contains scarcely a trace of sulphate.

On precipitating in the cold, I obtained, instead of a very white and light powder, a heavy product of a horny appearance. This does not appear to occur always; the way to prevent it is to precipitate while boiling and with weak ammonia. The dried product is remarkably light and white, but then it is the hydrated oxide, and not the oxide of zinc. It is easily reduced to the state of oxide by calcination, but then while retaining its lightness and extremely fine state of division, it presents that yellowish tint which oxide of zinc that has been strongly heated invariably exhibits. However, the precipitation of zinc by ammonia is a very excellent process, applicable to the preparation of oxide of zinc in the humid way.—*Journ. de Pharm.* for Jan. 1844.

Nitrate of Potash in Asthma.

A correspondent of the New-York Med. Gaz. states that he has derived essential benefit from using the following remedy in severe attacks of asthma, and has prescribed it for several patients with equal success:—

Immerse thick porous paper in a saturated solution of nitrate of potash, and hang it up to dry. At the approach of a paroxysm the patient may inhale the vapour by burning the paper in the room, or smoking it in a tobacco-pipe. The writer says he is acquainted with several asthmatics who are unable to breathe in a recumbent posture until their sleeping apartment has been filled with the above vapour. —*Lancet*, Jan. 6, 1844.

On the Preparation of Mercurial Ointment. By M. Fossembras.

There are few pharmaceutical preparations that have given rise to so many investigations and theories as mercurial ointment. So

much has been said on the subject, that anything new may at the very outset appear fastidious and useless.

It is with some hesitation therefore that I publish these considerations, which have suggested to me the employment of a process which allows of 8 lbs. of mercurial ointment being prepared in less than one hour. The process which I employ consists simply in the use of rancid fat, but it is so easy of execution that I have thought it right to rescue it from the oblivion into which it has fallen. Only 25 grms. of this substance are requisite for a pound of ointment, and so small a quantity is not capable of communicating injurious properties to a medicine which can never be preserved for any length of time from becoming rancid, and which is scarcely ever employed in any other state.

The requisite conditions for a prompt division of the metal may be reduced to two,—1st, dividing by trituration; and 2nd, preventing the reunion of the separated particles. The first condition is always complied with, but the second scarcely ever. In fact, fresh lard not possessing any agglutinative properties can for that very reason not retain the mercurial powder and prevent the reunion of its particles. Fresh lard therefore is incapable of extinguishing mercury in a perfect manner.

It may perhaps be objected, that a continued vigorous working is always followed in a short time by success; to which I would answer, that I have never seen the work terminated before the fat has acquired a rancid odour.

But why is this state of alteration of the fatty matter favourable to the extinction of the metal? The first thing that attracts our attention in rancid fat is its consistence. When it has been allowed to attain that degree of alteration at which it still possesses a certain softness, it will be perceived that it has acquired very marked agglutinative properties. When agitated in the mortar, it adheres strongly to the pestle. If a certain quantity of mercury is now poured into this triturated mass, and agitation continued, the metal is divided immediately, and the adhesion of the fat which surrounds each of the particles will necessarily prevent their reunion.

I will now relate the facts which prove the truth of the above considerations. I had exposed for some months to a moist atmosphere about a pound of fat; when I employed it, it was not hard, but it adhered strongly to the fingers. I took 200 grms., and triturated it for some minutes in a marble mortar, when it became soft like thick honey; I then poured 4 lbs. of mercury in portions of 300 grammes, and five minutes of trituration always sufficed for the complete extinction of the metal. After the introduction of the fourth portion the ointment had become somewhat hard, but the addition of a little oil of sweet almonds allowed of the operation being easily continued. In this manner I was enabled to incorporate 4 lbs. of mercury in the 200 grms. of fatty substance. Not the least metallic particle could be detected with the lens throughout the whole mass. I then added the 1800 grms. of recent lard in a state of semifusion, and after a quarter of an hour's trituration I ob-

tained a perfectly homogenous ointment, in which the mercury was extinguished most completely.

N.B. The above process is not very new, but it is eminently successful. It is similar to the method of MM. Coldefy and Simonin, which consists in extinguishing the mercury in a small quantity of lard, which has been prepared by melting it, pouring it into water, and exposing it to the action of the atmosphere.—*Journ. de Pharm.* for Jan. 1844.

Preparation of pure Cicutine and of the Sulphate. By M. Ville.

The plants of the Hemlock are collected just when they are about to flower; cleansed, stamped, and pressed as quickly as possible. About 1 per cent. sulphuric acid is added to the expressed juice, which is coagulated by heat and filtered immediately. It is then conveyed into a tubulated retort provided with a recipient, and evaporated one-half at a temperature not exceeding 176°. Upon this it is conveyed into a flask with two tubulures, the lateral one being provided with a cock, one-eighth of its weight of caustic potash added, and a volume of æther equalling that of the sap poured over it; after two hours the whole of the cicutine has separated, and is taken up by the æther, which is drawn off by the side tube and distilled in a retort at a gentle heat. The cicutine remains as a faintly-coloured oily fluid, of sufficient purity for medicinal purposes. To obtain it pure, it must be redistilled and the product collected in glass tubes, which are sealed immediately.

The sulphate however has great advantages over pure cicutine, both from its being possible to preserve it much longer and from its milder action. It is obtained in a form which keeps well, and is peculiarly adapted for employment by accurately neutralizing cicutine with dilute sulphuric acid, evaporating the liquid at 176° to the consistence of a syrup, weighing the residue, and adding to it an equal weight of white sugar.—*Bull. de Thérap.*, xxv. p. 282.

Mistura odorata, *or Fumigating Balsam, according to* L. Giseke.

48 ounces of alcohol of 0·833 spec. grav.,
4 ... Tinct. benzoes,
4 ... Tinct. Vanillæ,
¼ of an ounce of Tinct. moschi,
1 ounce of Æther aceticus,
½ an ounce of Bals. peruvian. nigr.,
½ ... Ol. macidis,
½ ... Ol. caryophyllor,
½ ... Ol. Cassiæ,
1 ounce of Ol. bergamotæ,
2 ounces of Ol. Cedræ,

are mixed together. The *Tinct. Vanillæ* is prepared for this purpose by extracting an ounce of comminuted vanilla first with 6 oz.

of *Spirit. vini rectificatus*, and then with 6 oz. of *Spirit. vini rectificatissim.*, and both tinctures mixed together.—*Archiv der Pharm.* for October.

A Specific against the Vomiting which occurs during Pregnancy. *By* Dr. Pitschaft.

Dr. Pitschaft has found the following pills, by numerous trials, to constitute a true specific means of curing the vomiting which torments pregnant women so severely at a certain period of utero-gestation:—

℞ Creosote, 15 centigrammes (= 2·31 English grains).
Hyoscyamus powder, q. s.
Distilled water, q. s.

Mix into a homogeneous mass, to be divided into 9 pills, of 10 centigrammes each, which should be covered with silver-leaf.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Improved Method of bleaching Palm Oil. *By* Charles Cameron, Esq.

About six years ago a process for discharging the colouring matter of palm oil was introduced into the soap-manufactories of Liverpool, which was as follows:—Into a strong cast-iron pan (built in the usual way, with a furnace below it) the manufacturers put 2, 3 or more tons of oil, according to its capacity; they then, by means of the fire below, increased the temperature of the oil to 450°; the result was, that the colouring matter was completely destroyed. But after working on it in the most careful manner, they were at last obliged to abandon it, for the following reasons:—

1st. By the time that the whole body of the oil was raised to 450°, the bottom of the boiler was heated to above 600°, and consequently the portion of oil in contact was decomposed, and being converted into gas, frequently caused explosions to take place.

2nd. The effluvium from the decomposed portion was insufferable.

3rd. If not immediately run off, on the colour being discharged, a black colour was frequently procured, from the charred oil being mixed with the other.

The process was cheap, but for these reasons, and the danger attending it, they were obliged to relinquish it.

I have stated the above, that you may the better understand the improvement I have effected in the process.

About four months ago I was induced to make some experiments to ascertain at what point of temperature the colouring matter began to give way, when I satisfactorily found that it began to change at 230°; and on continuing the process within 2° or 3°, more or less,

of that temperature, with *continued agitation*, it gradually lost its colour, and at last became as white as home-made tallow, and of a hardness superior to any imported. I then fully established the fact, that a low temperature (230° instead of 450°), length of time, and agitation (agitation was not employed in the old process), removed all the difficulties that prevented its former success.

The process which I recommend, and which is now acted upon here, may be thus described:—A cast-iron pot is provided, containing from 3 to 4 tons of oil, with the ordinary furnace below it, and a horizontal revolving fan of sheet-iron placed within it for agitation, power being obtained from a steam-engine with a speed of six revolutions per minute. In the absence of an engine, a wooden rake may be employed. The oil is then, by means of the fire, raised to a temperature of 230°; the fire is then withdrawn from below, and high-pressure steam is introduced from a boiler (15 lbs. pressure on the square inch of the valve), by means of the leaden pipes, two or more (according to the size of the boiler) of two inches diameter. By this means an equable temperature of 230° is obtained, without any danger of decomposing the oil, and the process is continued until the colour is completely gone. A vessel containing four tons will require ten hours to complete the process, at the expense of 2 or 3 cwt. of slack to each ton of oil.

It appears to me that the colouring matter is discharged by the absorption of oxygen from the atmosphere, as oil at a high temperature is known to have a strong affinity for oxygen, and hence agitation is essential, so as continually to present a new surface.

My process discolours a ton of oil here at 2*s.* per ton. Watt's process (formerly acted on) cost 20*s.* per ton.

[The above article is taken from the recently published *Transactions of the Society of Arts.*]

On the Desulphuration of Metals in general, applied to the Preparation of Sulphuric Acid, and especially to that of the Oxide of Antimony. *By* M. Rousseau.

The importance attached to the application made by M. de Ruolz, of the oxide of antimony as a substitute for the carbonate of lead in its various applications to the arts*, induces me to publish some results to which I have arrived respecting the desulphuration of metals, and especially the details of the process adopted by M. de Ruolz. Hitherto the only means employed in metallurgy to separate sulphur from the various metals, consists in roasting the ores for a more or less considerable time; but in whatever manner the operation may be conducted, the separation of these elements is never completely effected.

There is another method of desulphuration, in which both metal and sulphur are oxidized at the same time, converting the sulphuret into sulphate. It is a well-known fact, that when mineral sulphurets,

* See page 54 of the present volume.

piled in heaps, are exposed to the action of the atmosphere, gradually a slow combustion of the elements is effected, the sulphur and the metal acquiring the oxygen necessary to form a sulphate. The loss of time and inconveniences which attend this method has justly prevented its being employed in metallurgical operations. However, from the observation of this simple and natural fact, I have been led to examine into the action exerted by air and water *combined*, at a more or less elevated temperature, on the various sulphurets. The following are the results which I have obtained, not only in laboratory experiments, but on masses of several thousand kilogrammes.

The whole of the sulphur is converted into sulphurous acid, and the metal remains in the state of oxide entirely desulphurized, with this remarkable particularity with regard to the sulphurets of iron and of copper, that the fragments, while retaining their primitive form, increase considerably in volume; they are, so to say, disintegrated in their molecular arrangement, and are broken by the least pressure. If it is desired to collect the sulphurous gas, and to employ it in the manufacture of sulphuric acid, it is merely necessary to establish a communication between the apparatus in which the combustion of the ores is carried on and the leaden chambers.

From these results, pyrites, so abundant in some districts, and what is of far greater importance, ores, poor in metal but abounding in sulphur, as certain sulphurets of copper, may be turned to account either as sulphur ores or as oxides.

The above sufficiently explains why M. de Ruolz has given the preference to this mode of preparation for obtaining the oxide of antimony by simply employing the native sulphuret. The oxide of antimony resulting from this process is of the most beautiful white, and is in the state of an impalpable powder; it may therefore be immediately employed in painting without pulverization or grinding. This substance, produced in this manner under the influence of steam, is reduced to a degree of tenuity which it is impossible to obtain by any other means; and, what is most important, this mode of preparation would obviate the greater portion of chances of disease.—*Comptes Rendus*, Nov. 20, 1843.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Dec. 4, 1843. (The President in the Chair.) The following communications were read:—

"Note on a Paper on Ferric Acid, read May 16th, 1843," by J. D. Smith, Esq.

In this note Mr. Smith points out two errors which he has discovered in continuing his experiments on ferric acid, since the publication of his paper on that subject*. These errors have arisen from the presence of oxide of manganese in the sesquioxide of iron

* See this Journal, vol. i. p. 441.

of commerce, which was employed for the preparation of the ferric acid. The green salt of potash, described as another oxide of iron, the author now considers to be due solely to the presence of manganesious acid.

"On the circular Polarization of Light by transmission through Fluids," by Dr. Leeson.

Dr. Leeson laid before the Society the result of his experiments on this subject, which differ most materially from those of other able and acute observers. His experiments greatly narrow the application of this branch of optical science to the exigencies of chemical investigation. The point in which his experiments differ from those of other observers, is in regard to the possession of opposite rotations by fluids which have the property of deviating the plane of polarization of a beam of polarized light transmitted through them; some fluids being said to have a right-handed, others a left-handed rotation. The result of his experiments, made upon a great variety of fluids, particularly those said to possess opposite rotations, is (with one exception, viz. oil of lavender) that all such fluids deviate the plane of polarization in one direction only, viz. towards the right-hand. Dr. Leeson obtained an apparatus from M. Solal of Paris, made according to Biot's own directions; with this apparatus he confirmed his former conclusions, and an examination of the apparatus itself has in some degree suggested the sources of the error. Dr. Leeson briefly explained what was meant by the circular polarization of fluids. He then entered minutely into the methods he adopted of ascertaining whether the rotation is right or left-handed, by means of the apparatus which he exhibited, and by diagrams. Dr. Leeson submitted to the Society for examination, specimens of oil of turpentine and oil of lemons, two fluids said to possess opposite rotations, and concerning which there could be no mistake; and also specimens of right and left-handed quartz, where this difference of rotation undoubtedly existed, as a proof of the correctness of his observations.

Dr. Leeson concluded with a few observations calculated to elucidate the causes which led to these discrepancies of observation, and gave an explanation of the apparatus which he employed for the examination of the polarization of light through fluids, which apparatus separates the images more widely than the one used by Biot, and is so arranged that the ordinary ray always preserves its central position, whilst the extraordinary ray revolves round it; on the contrary, in Biot's arrangement, the two images dance round each other, and are thus easily confounded. This may have been one source of error, as of course all observations as to the rotation of the plane must refer to one image.

Dec. 18, 1843. (The President in the Chair.) The following communications were read:—

"Observations on Catechuic Acid," by John Thomas Cooper, Esq

Mr. Cooper commenced his observations by describing the tanning process to which his attention had been directed, and in which catechu is employed as the tanning agent. Upon completion of this

process, a whitish matter exudes on the surface of the leather; and it is the uniform appearance of this substance over the whole of the hide which is considered as a test of its perfection. The author then described his examination of this substance, which he found to consist principally of catechuic acid.

Analyses of catechu and cutch were appended to the paper.

"On a curious change in the Molecular Structure of Silver," by Robert Warington.

The subject of this communication was part of a silver funeral vase, dug up by some labourers about seven feet below the surface of the ground, between Bow and Stratford, while excavating brick-earth. It was put into the author's hands by Mr. Porrett, as bearing on the subject of alteration in molecular structure after solidification. It was extremely rotten and brittle, and presented under the microscope a highly crystalline structure, with a film of a totally different aspect on its exterior surface. After being heated to redness for a short time, it became totally altered in its characters, having lost its extreme brittleness, and presenting a tough, minute, granular structure; its specific gravity had also increased. On analysis it was found to contain chloride of silver, which separated in small flakes after the action of dilute nitric acid, and evidently constituted the superficial film observed under the microscope. The formation of this chloride must have arisen from the action of soluble sulphates and chlorides present in the soil from which it was dug, and this probably assisted by the presence of peroxide of iron existent in the brick-clay, and with which the surface of the metal was partially stained.

Meeting of the Royal Institution.

Friday, Jan. 19, 1844.

The evening meetings of the members of this institution commenced for the season on Friday with a lecture by Professor Faraday. The theatre was crowded to excess by the members. Mr. Faraday, after apologizing for having on this occasion nothing to offer beyond speculation, remarked upon the ready credence afforded to theories, particularly to the atomic theory, which he feared, by misleading, had very greatly checked the advance of science. By taking any solid body, as sulphur or copper, and submitting it to certain processes, as powdering, sieving, &c., the particles could be rendered so minute as to be undistinguishable by the eye; yet these particles, when united together, each particle in close contact with particle, formed the mass. This was perfectly clear, but when heat or cold is applied, the particles thus in contact are forced by heat to become more distant, the body becomes larger; the fluid in a thermometer was shown to rise, a bar of copper to become lengthened, when heat was applied to them; while, by the application of cold, the particles supposed already to be in close contact were still further drawn together, as was evident from the fluid in the thermometer and the bar of copper occupying a smaller space when cooled

with ice-cold water. But to introduce into chemistry this theory was attended with even more manifest contradictions. In a salt of iron the iron was combined with 1 atom of oxygen; by the addition of nitric acid and a slight application of heat half an atom additional became absorbed; but the word atom signified that which was indivisible. Yet a very distinct change had taken place, the colour was changed, and a very different precipitate would be observed on the addition of prussiate of potash. Mr. Faraday regarded also as an extremely inconvenient result of this theory, that in 1 atom of bile, supposed by the followers of this theory to be indivisible, 100 atoms of other bodies were enumerated in its composition. By the still further application of heat greater changes were produced; in spermaceti the particles no longer held together, they could be observed to move freely upon each other—in other words, the solid became liquid. By a still further application of heat the particles became aëriform, each molecule being very greatly removed from the other; he believed that the supposed space between the particles did not exist; that though the centres might be reduced to a mathematical point, still the circumferences would be in contact.

Electricity offered a very effective mode of testing this, as the particles of some bodies attracted while those of others did not. A stick of shell-lac was shown not to conduct, while a bar of copper conducted instantaneously. With voltaic electricity a constant current could be easily maintained, and the conducting powers of the various metals contrasted, and it would be at once seen that this power of conducting did not depend upon any closeness of contact among the particles, for platinum, a metal of very high specific gravity, conducted less freely than copper; and potassium, which conducted electricity, when oxidized did not conduct, though from its then occupying but a third of the space the particles must be in closer contact. Several experiments to illustrate these facts were shown by Grove's battery.

[This highly curious lecture is published entire in the Philosophical Magazine for the present month, to which journal we may refer our readers, as it is impossible to do justice to it in an abstract.]

PATENTS.

Patent granted to Arthur Dunn, Rotherhithe, Surrey, *for Improvements in treating, purifying and bleaching Oils and Fatty Matters.*

The invention relates to causing oils and fatty matters to be subjected to streams of atmospheric air forced below the surface thereof, so that the air rising to the surface will agitate the same and carry off impure odours, and at the same time bleach the oils or fatty matters under process. In carrying out the invention, the fatty matter or oil which it is desired to treat, bleach and purify, is to be kept heated,

by steam-pipes or other means, to from 170° to 230° Fahr., in any convenient vessel, over which should be placed a hood opening into a chimney, so as to conduct off any vapours which may arise into the outer atmosphere; and by means of perforated pipes, or perforated shallow vessels placed at the bottom of the vessel, numerous streams of air are forced through the oil or fatty matter, by any convenient blowing apparatus, into the perforated pipes or vessels, or the air may be forced into and below the fatty matter or oil by numerous small tubes, descending from one or more main tubes above the liquid matter in the vessel, such main pipe or pipes being in connexion with the blowing machinery or apparatus used. The air is employed at atmospheric temperature, it not having been found that the heating of the air used, before it is forced below fatty matters or oils, produces more beneficial results than air not heated. The time of operating on different oils and fatty matters will be found to vary from each other, and such is the case with respect to similar descriptions of oils and fatty matters; but as the result of the process of treating oils and fatty matters by air is progressive, and the extent of effect or result produced readily judged of from time to time, the workman will judge from samples taken out of the vessel, whether the oil or fatty matter is purified and bleached to the degree desired, and if not, he will continue the process of forcing air through the same till the desired result is obtained. The process is found to be quickened in some degree by the higher degrees of temperature, up to the highest temperature above mentioned; but it is considered desirable not to use higher temperatures than those mentioned, as fatty and oily matters may be injured by high temperatures, and where time is not an object a temperature of 200° Fahr. should not be exceeded.

The treating of oils and fatty matters with streams of air forced through or amongst the same, owing to the agitating effect produced, will be found useful when mixing fatty matters and oils with other matters, as the same will be very readily and intimately mixed.—Sealed March 28, 1843.

Patent granted to James Boydell, Jun., Oak-farm Iron-works, near Dudley, *for Improvements in manufacturing Bars of Iron coated with other Metal.*

This invention relates to a mode of rolling iron into bars, and in such manner that, the piles being properly prepared, the bars produced are covered externally with steel, by which means iron bars are produced applicable to a great variety of purposes, particularly in cases where articles of manufacture or parts of machinery require to have hard or polished surfaces; for instance, piston-rods, and the other smaller working parts of steam-engines, the shafting and other moving parts of machinery, or parts of machinery required to be kept bright and polished. The polished fire-bars and other parts of stoves, also fire-irons, and parts of fenders, and in fact such manufacture of bars of iron will offer all the toughness of iron with the

hard, and if polished the bright surface of steel, and will be useful where those properties are desired.

In carrying out this invention, the iron which is to be rolled into bars, of any desired section, is so piled that the external surfaces of the pile is formed of slabs, or bars, or pieces of steel, the thickness of steel in respect to the quantity of iron in a pile, depending on the thickness it is desired to have the steel on the bar rolled from such pile of iron with steel, such steel being used as may be best applicable for the purposes for which the bars manufactured therewith may be required. Having made up a pile with iron on the interior and steel on the outer surfaces, it is heated in a furnace as if it were simply a pile of iron; but in cases where a very thin coat of steel, or that of a very hard nature, is required upon the iron, the steel is added to the iron when it is partially heated, and when the steel and iron are at a welding heat, the heated pile is passed between grooved rollers till the figure of bar desired is obtained, whether the section be round, square, or otherwise.—Sealed April 7, 1843.

Patent granted to John Michell, Calenick, Cornwall, *for Improvements in extracting Copper, Iron, Lead, Bismuth, and other Metals or Minerals from Tin Ore.*

This invention consists in separating from tin ore the small quantities of copper, iron, lead, bismuth, and other metals or minerals mixed with it, and which, although existing in very small quantities, materially affect the quality of the tin; this is effected by dissolving them in such acids as will not act injuriously upon the oxide of tin.

The tin ore is pulverized, as usual, and the greater portion of the matrix separated by washing; it is then (by preference) calcined, and afterwards treated with acid, to dissolve the foreign metals or minerals, which may then be readily washed away. The best time for submitting the ore to the action of acid is before it becomes cool, after removal from the calcining furnace; and it should be allowed to remain in the acid for three or four days, or for a longer period if found necessary.

Muriatic acid is preferred by the patentee, diluted with an equal quantity of water, and employed in the proportion of one hundredweight of the ordinary acid of commerce to each ton of ore.

When the foreign metals are in the state of oxides, it will not be absolutely necessary to calcine the ores before operating with acid; and in some cases it may be desirable to apply heat, to expedite the process and lessen the quantity of acid employed, by putting the ore and acid into earthenware vessels, heated by a sand-bath.

The patentee does not confine himself to the use of liquid acid; as the acid evolved in the state of vapour, by various processes, may be employed. He claims the mode of purifying tin ore, by extracting foreign metals or minerals, by dissolving them in acid, and washing them off, or separating them, as above described.—Sealed April 11, 1843.

THE CHEMICAL GAZETTE.

No. XXXII.—February 15, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Combinations of Nitric Oxide with Muriatic and Fluoric Acids.

By Hugo Reinsch.

It has long been known that when muriatic acid is prepared with sulphuric acid containing nitric acid, the acid obtained is contaminated with chlorine; the same happens when nitric oxide is contained in the sulphuric acid, which is now frequently the case. From this it appeared impossible to obtain a combination of this base with muriatic acid. The first experiment which the author performed consisted in distilling a mixture of muriate of soda with crystallized sulphate of nitric oxide; at first some free nitric oxide was disengaged, but subsequently a yellow gas passed over, which did not appear to be very soluble in water, as it was not immediately absorbed like muriatic acid gas. The experiment was varied by passing muriatic acid and nitric oxide gas at the same time into a large glass flask provided with a cork having three perforations. The tube for conveying the nitric oxide reached to the bottom of the flask, while that for the muriatic acid was about half an inch from the bottom, so that the nitric oxide was compelled to force its way through the current of the muriatic acid gas. Into the third aperture of the cork was fitted a conducting tube, which terminated under water, to convey off the gas; the flask had been previously rinsed with water, so that its sides were moist. At first muriatic acid gas was allowod for some time to pass into the flask in order to expel the atmospheric air, upon which an equal current of nitric oxide was conveyed into the flask. The air had not been entirely expelled, since yellow vapours formed. After the two gases had been allowed to pass for some hours into the flask, an oily, yellowish-green liquid had formed, the water in the glass in which the excess of gas made its exit had become converted into a reddish-yellow liquid resembling fuming nitric acid, and the whole vessel was filled with a yellow gas which possessed a chlorine-like odour. Upon this the oily liquid in the flask was conveyed into a glass, and in this operation it was found that the conveying tube for the muriatic acid was coated for an inch near the aperture with colourless acicular crystals, which on being immersed in water dissolved with considerable effervescence and evolution of nitric oxide, and was certainly a crystalline compound of nitric oxide with muriatic acid. The yellow glass in the flask was decidedly not chlorine, but the vapour of gaseous muriate

of nitric oxide, as was proved by analysis; for when it was shaken with water it dissolved, and the solution acted on nitrate of silver and on protosulphate of iron; the gas moreover reddened blue litmus paper.

The oily greenish-yellow liquid had a milder taste than that of concentrated muriatic acid, and was much less acrid; it reddened litmus-paper, and was so volatile that it evaporated continually at a temperature of 46°, and forced the glass stopper out; when a drop was poured into a solution of sulphate of iron, this was immediately rendered black; and when thrown on small crystals of green vitriol covered with water, nitric oxide was given off with effervescence, and the crystals were converted into a brownish-black liquid, from which a powder of a similar colour was deposited, probably consisting of the peculiar combination of nitric oxide with the protoxide of iron, but which could not be isolated; for when brought into water, in order to wash it, it dissolved with effervescence and evolution of nitric oxide. Nor could it be isolated by adding alcohol to the protosulphate of iron, and then the muriate of nitric oxide; a black precipitate gradually formed, which however dissolved in alcohol of a brown colour, and was less easily decomposed in this solution than in the aqueous one; it could not be precipitated by æther from the alcoholic solution, but formed a dark green æthereal solution, which resisted longest the action of the atmosphere. As soon as water was added to the alcoholic æthereal solution, æther separated, and the liquid again became brown.

After the muriate of the nitric oxide, and also the aqueous solution in which the gas had been received, had been left undisturbed for several days, and was then submitted to examination, the latter was found to contain hardly any nitric oxide; it gave rise to a scarcely perceptible brownish tint with solution of sulphate of iron; blue litmus-paper was instantly bleached both in the gas and in the liquid; it had therefore become converted into chlorine. The gas of the oily compound reddened blue litmus-paper at first, and subsequently bleached it; the liquid acted in the same manner; it still imparted a brown colour to a solution of the sulphate of iron, but not to such an extent as at first. When, for instance, muriate of nitric oxide is poured over small fragments of yellow prussiate of potash, this is converted into a white spongy mass without there being any disengagement of nitric oxide or the liquid becoming brown; on adding some water to this mixture, a white powder is deposited, the liquid gradually becomes brown, and retains this colour for several days, while prussian blue is deposited on the sides of the vessel.

Fluoric Acid and Nitric Oxide.—The author prepared a considerable quantity of the sulphate of nitric oxide, by conveying an ounce of sulphuric acid into a small tubulated retort, through the tubulure of which the tube for conveying the gas was passed, and the neck of which fitted into a tubulated recipient, which also contained sulphuric acid; the tubulure of the recipient was merely covered with a funnel, so that it communicated with the external atmosphere.

For disengaging the gas, ordinary nitro-muriatic acid diluted with one-fourth part water was employed; this affords a very equal and constant current of gas. The sulphuric acid in the retort became bluish after the gas had been passed through for a quarter of an hour, although it was by no means wholly absorbed even when the gas-bubbles followed each other slowly; but by far the greater portion passed over into the recipient, where it absorbed oxygen and became converted into nitrous acid, which was rapidly absorbed by the sulphuric acid contained in the recipient, which immediately became covered with a pellicle of crystals, that had frequently to be broken by shaking in order to allow the gas to act. After some time the sulphuric acid assumed a violet, and at last a dark violet colour. Having now to renew the nitric acid in the disengaging flask, and the current being at first somewhat violent, a very remarkable reaction ensued; the acid became completely colourless in a few instants, but after the evolution of gas for several hours the acid had again assumed the dark violet colour. The acid in the retort was perfectly liquid; after passing gas into it for eighteen hours not a trace of crystallization was to be seen, while the acid in the receiver, containing nearly as much as was in the retort, had become converted into a white mass of crystals. It is therefore certain that the sulphate of nitric oxide is most easily formed with the intermediation of atmospheric air. After the evolution of gas had ceased, the retort as well as the recipient were closed air-tight. For eight hours during the night the acid in the retort had retained its violet colour; on slightly moving the retort, the acid lost, as by magic, its violet colour, and appeared yellowish. It did not crystallize even when exposed to the action of the atmosphere, although it was very highly charged with nitric oxide. The author now conveyed a portion of finely-pulverized fluor-spar into a glass flask provided with a glass escape-tube, in which was contained half a part of the sulphate of nitric oxide; shook the mixture and exposed it to heat; at first some nitric oxide was disengaged, subsequently some fluoride of silicon. As there was a decomposition the operation was effected in a leaden retort, and the gas collected in a leaden vessel containing some water; in the present instance no nitric oxide was evolved, and the gas which passed over was absorbed with a hissing noise by the water; neither the aqueous solution nor the vapours evolved had a bleaching action on blue litmus-paper, but only reddened it, showing therefore that no free fluorine is given off; the liquid coloured green vitriol brown. What becomes in this experiment of the nitric oxide of the sulphate? Does it decompose the fluoric acid partly into fluorine, which latter immediately combines with the lead? An experiment to combine the two gases in a leaden vessel likewise proved unsuccessful.—Buch. *Rept.*, xxxii. p. 164.

On Liebig's Theory of Gout. By Dr. Todd.

It is affirmed by Liebig that the presence of lithic acid in the system is due to the deficiency of oxygen; that in the natural state,

under the influence of a due supply of oxygen, this substance nearly or altogether disappears, being decomposed by oxygen into urea and carbonic acid; so that in healthy urine its quantity is very small, and in the carnivorous animals, which are largely supplied with oxygen, it disappears altogether. The free acid which exists in the system is said to be lactic acid derived from the stomach, and it is further added that this and other non-nitrogenous compounds present in the blood attract the oxygen and hinder its action upon the lithic acid.

Were this theory true, two conclusions must flow from it;—1st, that under all circumstances where oxygen is abundant lithic acid shall be absent and urea exist; and 2nd, where oxygen is deficient lithic acid must be present and urea deficient; or that in either case the quantities of the lithic acid and urea must be in an inverse ratio.

Now it appears, from the analysis made by M. Becquerel of the urine in various diseases, that such a relation of quantity between these two important elements does not exist. He finds that in many cases of fever the quantity of urea is very slightly diminished below the natural standard, and that the normal proportion of urea to lithic acid is but little changed; whilst in chlorosis and anæmia, diseases where the deficiency of oxygen is obvious, lithic acid, which ought to be increased, is diminished, and in the former of those diseased states it is reduced to a minimum, and the urea is diminished also.

In Bright's disease, in which the urea is so often diminished *in the urine*, the lithic acid ought, according to Liebig, to be increased; but such is certainly not the case in the great majority of instances; on the contrary, it is very generally much diminished. And when we reflect on the anæmic, cachectic appearance of the class of persons who are for the most part the subjects of this disease, we cannot fail to perceive that their system is greatly deficient in oxygen, a condition which, according to this chemist, ought to have left a considerable quantity of lithic acid undecomposed.

Again, according to this theory, the existence of the lithates is incompatible with that of the phosphates in considerable quantity in the same urine; for the production of the latter, if Liebig's views be correct, is due to the very cause which ought to occasion the disappearance of the former, namely, an abundant supply of oxygen. But I can aver, from my own experience, that phosphates and lithates may coexist in urine in great abundance. In such urine it sometimes happens that the lithates are not deposited on cooling; but the phosphates are precipitated as a cloud, which becomes greatly increased on the addition of ammonia or by heat; or if, instead of ammonia, a few drops of nitric acid be added, a copious precipitate takes place of lithate of ammonia, which is readily dissolved by heat*.

* This observation of Dr. Todd is incorrect: lithate of ammonia is under no circumstances precipitated by nitric acid, nor could it be so, as it is at once decomposed by it.—Ed. *Chem. Gaz.*

Moreover, an excess of urea and an excess of lithic acid ought not to exist together; but that they may so exist, I have positive proof in the urine of a patient at present under my care, which, with a specific gravity of 1030 deposits lithate of ammonia copiously, and yields nitrate of urea in large quantity immediately on the addition of nitric acid.

It is remarkable that the two classes of animals which are most highly oxygenated are deficient in urea and secrete lithic acid in abundance. These are birds and insects. In the former animals, as Dr. Golding Bird has remarked, respiration is very perfect; their animal heat is superior to that of man, and their hearts pulsate much more quickly; their system must therefore be freely supplied with oxygen. In them therefore no uric acid ought to escape unchanged, yet the truth is that the acid is excreted nearly as abundantly as in serpents. "The semi-solid urine which escapes from the cloaca of the jackdaw, parrot, and many other birds, contains a large proportion of urate of ammonia."

In insects the lithate of ammonia may be seen in the Malpighian vessels or kidneys, as many observers have found, and as I can affirm from my own observation; and, I may add, that the case of insects is still more opposed to the doctrine of Liebig than that of birds, for in them the oxygen is brought to every part of the body by the numberless ramifications of the tracheæ, and even to the walls of the tubes, by which the excretion is effected.

In the present state of our knowledge it seems impossible to determine the correct theory of gout. It appears highly probable however that the peculiar gouty matter is in the first instance derived from the stomach or duodenum, inasmuch as a disturbance of the functions of those parts is an invariable antecedent or accompaniment of the fit; and as such derangements are generally accompanied with an undue development of lactic acid, an acid nearly resembling the acetic in its constitution and properties, it seems fair to conclude that it may be the primary disturbing agent. Again, the habits of life of those in whom the gouty diathesis occurs are such as to favour the generation of lithic acid. And lastly, as the liver is deficient in its action in those cases, it may be conjectured that soda is imperfectly eliminated from the blood, and may accumulate in the circulation to unite with lithic acid, wherever that may be formed in the secondary destructive assimilating processes.

The cases which I have adduced of gout appearing in low states of the system, show that the morbid element of the disease may be present independently of lithic acid, for in them this substance either did not abound, or did not exceed the normal quantity by a greater amount than may be at any time caused by a slight general disturbance.

It appears to me that we must look for the matter of gout as a compound derived from a product of unhealthy action of the stomach and duodenum, which being absorbed into the blood, unites there with some element of the bile which has been suffered to accumulate through the defective secretory action of the liver.

As the same causes which induce these two states will give rise to a lithic acid diathesis, we find it usually associated with them; but the former may exist without the latter, and therefore gout may show itself without the occurrence at the same time of a preternatural quantity of lithic acid.

An organic compound, such as I have conjectured, may exist in the blood in variable quantity and for an indefinite period, contaminating the whole frame and the offspring from it, and may thus give rise to the gouty diathesis. Or this matter, ever present in the system, may be liable to periodical accumulations, which can only be got rid of by periodical paroxysms.—From Todd's *Practical Remarks on Gout, &c.*

On crystallized and liquid Cedar Oil (Cedrene). *By* P. H. WALTER.

The crystalline portion of the true cedar oil may be readily purified by frequent recrystallization from alcohol; it should be of a brilliant white, without the slightest tint of green. It was melted and submitted to analysis with oxide of copper and chlorate of potash, with the following results:—

	Found.	Atoms.		Calculated.
Carbon	81·0	32 =	2400	81·3
Hydrogen	11·8	28 =	350	11·8
Oxygen		2 =	200	6·9
			2950	

The specific gravity of the vapour was found to be 8·4; according to theory it is 8·27.

It is not possible to obtain the liquid portion of the cedar oil or the cedrene perfectly pure by distilling it several times over phosphoric acid; it is necessary to have recourse to potassium, over which the oil is distilled until the metal no longer becomes coated with a red pellicle, and the cedrene passes over colourless. Submitted to analysis it afforded the following results:—

	Found.	Atoms.		Calculated.
Carbon	87·99	32 =	2400	88·05
Hydrogen	11·95	26 =	325	11·95
	99·94		2725	100·00

The density of the vapour, calculated according to this formula, $\frac{30{\cdot}55}{4} = 7{\cdot}64$, the experiment afforded 7·9.

The author has also examined natural cedrene, and distilled it several times over potassium, until the latter was no longer covered with a pellicle, but retained its lustre. In this manner it is obtained colourless, and with the same characters and the same boiling-point (480° Fahr.) as the artificial cedrene. Submitted to analysis it afforded 87·8 C and 12.01 H; they are therefore perfectly identical. —*Ann. de Chim. et de Phys.*, vol. viii. p. 354.

Researches on Lanthanium. *By* R. Hermann.

Separation of Lanthanium.—The pulverized cerite is treated in precisely the same manner as described by the author in the preparation of the oxide of cerium*. The solution obtained by digesting the ignited oxides with dilute nitric acid, and filtered from the impure oxide of cerium, is saturated with ammonia, as much of the latter being added as possible without producing a permanent precipitate, after which phosphoric acid is added to the liquid, which is then warmed. A white pulverulent precipitate of phosphate of lanthanium is formed, while alumina, lime, magnesia and oxide of manganese, in combination with phosphoric acid, remain dissolved in the acid liquid, and may be separated on the addition of ammonia as phosphates. The phosphate of lanthanium is now free from any mixture of earth, but it still contains oxide of cerium. To separate it, the dried phosphate of lanthanium is mixed with double its weight of carbonate of soda and heated to redness. On digesting the ignited mass with water, ceriferous oxide of lanthanium remains undissolved. It is dissolved in nitric acid diluted 100 times, when the oxide of cerium remains undissolved. The filtered solution is evaporated to dryness, the nitrate ignited, the oxide again dissolved in dilute nitric acid, and these operations repeated as long as oxide of cerium remains behind on dissolving the oxide of lanthanium. In this manner an oxide of lanthanium is obtained, in which not a trace of cerium can be detected by reagents. This oxide of lanthanium is dissolved in sulphuric acid and crystallized, when a bright rose-red prismatic salt in radiant groups is formed of perfectly pure sulphate of lanthanium†. The author states that he could not detect the least trace of didymium in his researches on cerite.

Atomic Weight of Lanthanium.—240·22 parts of dried sulphate of lanthanium gave 219·61 parts of ignited sulphate of barytes. The atomic weight of the oxide of lanthanium is, according to this, 700; and supposing the oxide to contain 1 atom oxygen, that of lanthanium will be 600, considerably higher therefore than found by Choubine and Rammelsberg.

Oxide of Lanthanium.—Lanthanium appears to combine with oxygen only in one proportion. Oxide of lanthanium dissolves in muriatic acid without disengagement of chlorine, and forms a salt, the amount of chlorine in which corresponds to the amount of oxygen in the oxides obtained by igniting the nitrate, carbonate or oxalate of lanthanium.

The chloride of lanthanium contains 42·55 Cl. On substituting an equivalent of oxygen for the chlorine, the following composition of the oxide is obtained:—

* See p. 6 of the present volume.

† Mosander states that the salts of lanthanium are perfectly colourless, and that the amethyst colour is owing to the presence of the new metal didymium. —Ed. *Chem. Gaz.*

		Atoms.	Calculated.
Lanthanium	85·667	1 = 600	85·714
Oxygen	14·333	1 = 100	14·186
	100·000	700	99·900

The oxide of lanthanium, as obtained by ignition of the nitrate, forms a porous, dirty white mass of a silky lustre, which on being reduced to powder acquires a colour which approaches nearest to that of cork.

Before the blowpipe the oxide of lanthanium behaves in the following manner:—It does not fuse with soda, which is absorbed by the charcoal, and leaves the oxide behind as a dirty white mass. Borax dissolves it in considerable quantity. The bead is perfectly colourless both while hot and after cooling, and only when it has been saturated to an excess with oxide of lanthanium does the bead appear on cooling of a light rose colour, which is rendered perceptible by holding it against a white ground; it cannot be rendered opake by flaming. When the bead appears, while hot, of a yellow colour, it is a sign that the oxide of lanthanium still contains oxide of cerium, in which case it may also be rendered opake by flaming. It behaves towards microcosmic salt as towards borax.

Oxide of lanthanium is easily dissolved by the mineral acids, especially by sulphuric, muriatic and nitric acids, with which it produces rose-coloured salts. The solutions of salts of lanthanium behave towards reagents as follows:—Phosphoric and oxalic acids and their salts produce white precipitates, very slightly soluble in an excess of the acid.

Fluoride of sodium produces a white flocculent precipitate of fluoride of lanthanium. Sulphate of potash produces a white pulverulent double salt, which is of very difficult solution. Caustic ammonia affords white, gelatinous, transparent precipitates in solutions of salts of lanthanium, which are basic salts of lanthanium. The fixed caustic alkalies produce a reddish precipitate of the hydrated oxide of lanthanium, which is insoluble in an excess of caustic alkalies; it greedily absorbs carbonic acid from the atmosphere and becomes white. When the hydrated oxide becomes yellow by exposure to the atmosphere, it contains oxide of cerium, which acquires this colour when it is converted by the absorption of carbonic acid into carbonate of the oxide of cerium; when the precipitate becomes brown, the oxide of lanthanium contains manganese or peroxide of cerium. Carbonate alkalies added in excess produce white precipitates, insoluble in an excess of the reagent. Alkaline sulphurets behave like the caustic alkalies; they produce precipitates of the hydrated oxide of lanthanium. Sulphuretted hydrogen and tincture of galls cause no change. Ferrocyanate of potash produces a white precipitate.

Oxide of lanthanium has so strong an affinity to several of the earths and metallic oxides, that it can only be separated from them with great difficulty. This is especially the case with lime, mag-

nesia, oxide of manganese and oxide of cerium. Thus, oxide of lanthanium, when precipitated by caustic ammonia from a liquid containing lime, carries down some of the lime with it. In the same manner it combines with magnesia and oxide of manganese, without its being possible to prevent these admixtures by the addition of chloride of ammonium; nor can these bases be separated from salts of lanthanium by combining them with acids and crystallizing as they form double salts. A peculiarly remarkable double salt is obtained when the impure oxide of lanthanium, prepared according to Mosander's method, is dissolved in sulphuric acid, and the solution allowed to evaporate at a low temperature over sulphuric acid. An amethyst-coloured octahedral salt, having the composition of an alum, is formed, which principally consists of lanthanium and sulphate of the oxide of cerium, but in which a portion of the oxide of cerium is replaced by oxide of manganese, and a portion of the lanthanium by lime or magnesia. Along with this granular crystalline salt is usually found a light rose coloured prismatic salt, in radiate groups; this is pure sulphate of lanthanium.

Hydrated Oxide of Lanthanium is obtained by precipitating salts of lanthanium with the fixed caustic alkalies. It forms a reddish, gelatinous, transparent precipitate, which becomes darker on drying; it absorbs rapidly carbonic acid, and then becomes white.

Carbonates of the Oxide of Lanthanium.—A salt with 4 atoms of base to 5 of acid is obtained when sesquicarbonate of ammonia is added to a solution of a salt of lanthanium. It forms a flocculent precipitate, which becomes crystalline after some time. After drying by exposure to the air at a low temperature, it forms an extremely loose, light, laminar, crystalline powder of a silky lustre. It contained 67·56 per cent. LnO and 32·44 CO^2. The formula requires 67·06 and 32·94. The crystalline salt contains water in variable proportions, sometimes 4 and sometimes 5 atoms; it afforded, for instance, 9·55, and also 12·09 per cent. water.

Neutral carbonate of lanthanium is formed on precipitating salts of lanthanium with neutral carbonate of soda. It is a white flocculent precipitate, which on drying constitutes a white adherent powder resembling chalk. It contains 71·73 LnO and 28·27 CO^2; the formula LnO CO^2 requires 71·79 and 28·21; it contains no chemically-combined water, but only 3 per cent. hygroscopic water.

Carbonate of lanthanium with three atoms of base occurs native in the mineral, which was formerly considered to be the protocarbonate of cerium, and which Mosander proved to consist for the greater part of carbonate of lanthanium, and to contain only traces of oxide of cerium. The same compound likewise occurs in cerite, in combination with basic silicate of the protoxide of cerium.

According to M. Hisinger, the native carbonate of lanthanium consists of 75·7 LnO, 10·8 CO^2, 13·5 aq; the formula 3 LnO CO^2 + 3 aq requires 77·42, 10·13, 12·45.

Phosphate of Lanthanium, a white pulverulent precipitate, is obtained on adding phosphoric acid to solutions of salts of lanthanium; it is but very little soluble in the free acid, and dries to a white pow-

der, which easily coheres, and has then a roseate tint; it consisted of 70·96 LnO, 29·04 PO^5; the formula 3 LnO PO^5 requires 70·18 and 29·82.

Sulphate of Lanthanium.—Oxide of lanthanium dissolves easily in dilute sulphuric acid; the solution deposits on evaporation acicular prisms in radiate groups of an amethyst colour. The salt gives off water at a faint red heat, and becomes opake and white, but does not melt. At a strong red heat the salt loses a portion of its acid, and deposits on solution in water a white powder, whose composition corresponds to the formula 3 LnO + SO^3.

The anhydrous sulphate of lanthanium was found to consist of 58·28 LnO, 41·72 SO^3=LnO SO^3.

The ignited anhydrous sulphate of lanthanium dissolves readily in water, if it be conveyed in a finely-pulverized state, and in small portions, into cold water, and the liquid be constantly stirred, so that no salt can be deposited; when, on the contrary, water is poured over the ignited salt, it combines with its water of crystallization, with evolution of heat, and becomes difficult of solution.

The crystallized sulphate of lanthanium is likewise very sparingly soluble, and requires 25 parts of water to be dissolved. When a concentrated solution of ignited sulphate of lanthanium, prepared in the cold as above described, is warmed, the greater portion of the salt separates in the crystallized state, independent of the evaporization of the water.

The crystallized sulphate of lanthanium contains 22·2 per cent. water = 3 atoms.

Sulphate of Lanthanium and Potash.—When a solution of sulphate of lanthanium is mixed with a concentrated solution of sulphate of potash, a white crystalline precipitate separates, which is the sulphate of lanthanium and potash.

The compound contained only $1\frac{1}{2}$ per cent. hygroscopic water. The salt fuses at a red heat, and then acquires an amethyst colour. The sulphate of lanthanium appears, like the protosulphate of cerium, to combine in several proportions with the sulphate of potash.

Chloride of Lanthanium.—Oxide of lanthanium dissolves readily in muriatic acid; on evaporation over sulphuric acid, the salt crystallizes in trilateral prisms of an amethyst colour. The crystals are seldom found isolated; they generally occur in feathery or in radiate groups. The salt deliquesces by exposure to the atmosphere, and easily dissolves in alcohol, to the flame of which it imparts no colouring. The salt melts in its water of crystallization on being heated, gives off muriatic acid, and leaves behind a mixture of chloride and oxichloride of lanthanium, which latter is converted, on being brought into contact with water, into basic muriate of lanthanium. The chloride of lanthanium was found to consist of 57·45 Ln and 42·55 Cl; the formula LnCl requires 57·47 and 42·64.

The crystallized salt contains 32·9 to 33·3 per cent. water; 4 atoms require 30·14.

Basic Muriate of Lanthanium is obtained by igniting chloride of

lanthanium exposed to the atmosphere, and edulcoration of the calcined mass. It is a white powder, very difficult of solution in water, and consists of 83·0 LnO, 17·0 ClH; the formula 3 LnO + ClH requires 82·19 and 17·81.

Nitrate of Lanthanium is obtained by dissolving oxide of lanthanium in nitric acid. It crystallizes with difficulty, and forms a rose-coloured saline mass, which deliquesces by exposure to the atmosphere and dissolves in alcohol. The salt appears to crystallize in octahedrons; it contains no water of crystallization, and consists of 50·9 per cent. LnO and 49·1 NO^5; the formula $LnONO^5$ requires 50·83 and 49·17.

Oxalate of Lanthanium is obtained on precipitating salts of lanthanium with oxalate of ammonia; it forms a white powder. The salt, dried at 122° Fahr., left on ignition 47·50 per cent. oxide of lanthanium; it is therefore LnO, C^2O^3 + 3 aq, which requires 47·01 per cent. oxide.—*Journ. für Prakt. Chem.*, xxx. pp. 197–206.

On the Resins of Benzoin and the Products of their Decomposition. *By* M. Kopp.

The author has analysed benzoin according to the methods of Unverdorben and Stoltze, and has arrived essentially at the same results, with only this exception, that a small quantity of a fourth reddish resin was deposited in the course of some time from the æthereal solution of the alpha resin. The following are the quantitative results:—

	I.	II.
Benzoic acid	14·0	14·5
Alpha resin	52·0	48·0
Beta resin	25·0	28·0
Gamma resin	3·0	3·5
Fourth resin	0·8	0·5
Impurities	5·2	5·5

When benzoin resin is submitted to dry distillation olefiant gas is disengaged, and there remains in the retort a carbonaceous residue, while a butter-like substance condenses in the recipients, which may be separated imperfectly by pressing between blotting-paper, more completely by hot water, but best by dilute alkalies, into a substance soluble in alkali, and an oil which is not dissolved by them. The first substance is *benzoic acid*; the oil is *phenol*, since it affords with nitric acid carbazotic acid, colours fir-wood blue with muriatic acid, boils at 392°, coagulates albumen, and is $C^{12}H^6O^2$.

Four equivalents of resin = $C^{80}H^{44}O^4$ afford 3 equivalents of benzoic acid = $C^{42}H^{38}O^{12}$, 1 equivalent of phenol = $C^{12}H^6O^2$, 8C, 2HO and 18HC.

On treating the resins with nitric acid, they are violently acted upon with evolution of nitrous vapours, and in the recipient condenses hydruret of benzoyle, prussic acid, and some benzoic acid. On extracting the residue with boiling water a solution is obtained, which deposits on cooling a new yellow acid, benzoresinic acid.

The mother-ley still contains much of this acid along with cabarzotic acid*. The mixture is saturated with carbonate of potash, and placed aside to crystallize; the carbazotic salt first separates, and then the benzoresinic acid is precipitated from the concentrated mother-leys by an acid.

Benzoresinic acid is an amorphous yellowish-white powder of a pungent taste; it melts at 248°; at a higher temperature it volatilizes, being partially decomposed, and with formation of shining white laminæ; it is inflammable, and burns with a red smoky flame. It dissolves very readily in alcohol and æther; the solution turns blue litmus-paper red; it is dissolved without change by sulphuric, muriatic and nitric acids, and is reprecipitated by water. The alkaline salts are yellow and not crystalline; the potash salt however may be obtained in crystalline laminæ. The solution of the potash salt gives sulphur-yellow precipitates with salts of lead, brownish-yellow with salts of silver, bright green with copper, pure yellow with alumina, yellowish-white with persalts of iron, and yellowish-green with protosalts.

Benzoin affords with chromic acid, benzoic acid and hydruret of benzoyle; and with dried alkalies at an elevated temperature, an oil analogous to benzon.—*L'Institut*, No. 517.

On the Oil of Thuja. *By* E. Schweizer.

Oil of Thuja occurs in the common Lignum Vitæ, *Thuja occidentalis*. It is a mixture of at least two distinct oxygeniferous oils; a hydrocarbon does not exist in it. Recently prepared it is perfectly colourless, but it soon acquires a yellowish colour. It has the peculiar smell of Thuja, and an acrid taste; is lighter than water, and but sparingly soluble in it, but it is readily dissolved by alcohol and æther.

The oil freed from water by chloride of calcium from two different preparations exhibited the following composition:—

	I.	II.
Carbon	77·99	77·25
Hydrogen	10·73	11·11
Oxygen	11·28	11·64

On submitting the oil to distillation, it begins to boil at 374° Fahr.; the greater portion goes over between 380° and 387°, the thermometer rising very slowly; the product is colourless; from 387° the boiling point ascends more rapidly to 403°; what passes over now has a yellowish colour; there finally remains a small red-coloured residue. The portions collected at different temperatures exhibited the following composition:—

	At 380°.	380°–387°.	387°–403°.
Carbon	71·00	70·55	76·13
Hydrogen	10·61	10·76	10·67
Oxygen	18·39	18·69	13·20

* The author obtained the carbazotate of lead in beautiful yellow needles with 1 equivalent of water, which detonated violently by exposure to heat, by mixing concentrated solutions of acetate of lead and carbazotate of potash.

Hydrate of potash instantly colours the oil of Thuja blackish-brown; on distilling the mixture a portion of the oil passes over unchanged, the remainder is converted by the potash into a resinous mass. When that which has passed over is distilled repeatedly over fresh hydrate of potash, the distillate nevertheless always possesses the properties of the Thuja oil, but its quantity constantly diminishes. Oil of Thuja, rectified in this manner five times over hydrate of potash, contained C 78·87, H 10·98, O 10·15.

On treating the blackish-brown residue in the retort with water, a resinous mass separates, which is insoluble in the alkaline liquid, but dissolves readily in pure water. It is a combination of potash with an acid resin, which in its pure state melts easily, has a reddish-brown colour, is soluble in alcohol, and consists of two portions, one of which is precipitated by an alcoholic solution of acetate of lead without any addition of ammonia, while the other is only precipitated on the addition of this agent.

The alkaline solution, separated from the resinous compound, is rendered milky on saturating the alkali with an acid, and a small quantity of an oil separates, which from its properties is evidently *carvacrol.*

Iodine is dissolved in considerable quantity in oil of Thuja. On being heated in a retort a very violent action ensues, the liquid continues to boil after removal from the fire, very little hydriodic acid is given off, and an oil distils over, the odour of which is perfectly distinct from the oil employed. When the reaction has ceased, and it is heated further, a thick dark-coloured oil passes over; at last iodine vapours appear, and a black mass remains behind. If the easily-volatile product is submitted to frequent distillation over iodine, and then in order to purify it is distilled over burnt lime, and finally over potassium, a carburetted hydrogen *Thujon* is obtained. This is colourless, and possesses an odour resembling oil of turpentine, and an acrid taste; it is lighter than water, and boils between 329° and 347° Fahr. The composition of Thujon could not be accurately ascertained from want of sufficient substance to purify it completely.

When the thick oil is treated with a solution of potash, the greater portion of it is dissolved. What remains undissolved is distilled several times over burnt lime to remove any iodine. A peculiar oil of thickish consistence, yellowish colour, faint odour and mild taste, is obtained; it is lighter than water, and burns with a very sooty flame. From its always being produced only in small quantity, the composition could not be accurately determined. From one analysis it appeared to be a carburetted hydrogen, having much resemblance to colophene, which M. Claus obtained by acting on camphor with iodine.

Carvacrol separates on saturating the alkaline solution with an acid in considerable quantity; by distilling it several times over burnt lime it was obtained pure, with its peculiar properties.

The black mass which remains behind in the distillation consists of a dark reddish-brown resin, which is very soluble in æther,

scarcely soluble in alcohol, of an acid nature, and contains no iodine, and of a carbonaceous body insoluble in alcohol and in æther.

Oil of Thuja behaves therefore towards iodine precisely as camphor, according to the researches of M. Claus; the products of both reactions correspond, not only in their mode of formation, but also in their properties.

Oil of Thuja is not much altered on being submitted to distillation with phosphoric acid. Sulphuric acid converts it instantly into a resin. Potassium oxidizes in it without any disengagement of hydrogen, and converts it into a resinous mass.—*Journ. für Prakt. Chem.*, xxx. p. 376.

ANALYTICAL CHEMISTRY.

A new Method for estimating the Quantity of Carbonate of Lime present in Calcareous Substances. By J. Lawrence Smith, M.D.

Among the most ready methods used for the purpose of estimating the quantity of carbonate of lime contained in calcareous substances, are Davy's pneumatic and Rogers's methods, the one estimating it from the bulk of carbonic acid, and the other by the weight of the carbonic acid afforded by the action of an acid. The principal objection to the former is the complication of the apparatus, and for the latter it is necessary to be furnished with a more than ordinary pair of balances and a set of accurate weights, whereas the instrument about to be described is free from both these objections, with the additional advantage of affording more accurate results.

It appeared at first, that by taking a certain quantity of the substance to be examined, and letting fall upon it by degrees a solution of acid, the strength of which we know, that it might be possible to estimate the quantity of carbonate of lime in the same manner as the carbonates of the fixed alkalies are estimated; but for this to succeed it is necessary that the substance should be finely pulverized, and free from any materials soluble in the acid used; but as it is not common to be furnished with these two conditions, another method had to be adopted, the principle of which is to treat the calcareous substance with an *excess* of acid, the strength of which is known, and then to find out the amount of this excess, thereby knowing the quantity of acid taken up, from which we can easily calculate the quantity of carbonate of lime present. In the application of this principle it will be found that anything like difficult manipulation is avoided, and that there is no calculation required.

The first thing to be furnished with is an instrument which consists simply of a tube about half an inch in diameter and ten inches long, having the principal part of it graduated in one hundred parts, the extremity being drawn out and bent downwards, leaving an opening so small as to allow a liquid to flow but slowly from the tube. To the upper part, for convenience' sake, is adapted a per-

forated cork, with a small tube, for the purpose of regulating the flow of the fluid, by placing upon it and withdrawing from it the finger, as we may wish to arrest or allow the liquid to flow from the extremity. With this instrument, which I propose calling the *Calcarimeter* from its use, we must be furnished with two fluids, a solution of muriatic or nitric acid and a solution of ammonia, both of which are prepared of a certain strength*.

Preparation of the Acid Solution.—This solution is prepared as follows:—Weigh out 50 grs. of dry finely-powdered pure carbonate of lime, or what is better, carbonate of lime precipitated from any of its solutions by carbonate of potash or soda. Place this in a tea-cup or other convenient vessel, add to it about an ounce of water (this is done simply for the purpose of moderating the action of the acid), then take the muriatic or nitric acid of commerce, and dilute it with 1 part of water; with this liquid fill the instrument to the 100 point, then let the acid fall gently upon the carbonate of lime, so as not to create a too great effervescence, and by proceeding carefully with the aid of a piece of litmus-paper, we can find the exact point at which the carbonate of lime is all taken up by the solution having an acid reaction. When we see that nearly all the lime is taken up, we proceed very cautiously, by adding but a few drops of the acid at a time, and agitating the mixture considerably, for the purpose of bringing the insoluble carbonate well in contact with the different parts of the fluid. When the acid reaction commences, the acid is no longer added, and the point at which the acid now stands in the tube is marked, and by subtracting that from 100 we have the number of degrees of acid used to dissolve 50 grs. of carbonate of lime; but as it is desired that the liquid should be so made as to require 50° of it to dissolve 50 grs. of the carbonate, it is diluted with the proper quantity of water. For example, suppose the fluid marked 65° after the experiment; this indicates that 35° of the acid solution were required to dissolve the 50 grs. Now instead of 35° we require it to take 50° to dissolve the same quantity, so that by making up the difference between the 35° and 50° with water, the solution is prepared; that is to say, to every 35 parts of the acid experimented with 15 parts of water are added. The solution can be again tested if necessary, and slight modifications made.

Preparation of the Alkaline Solution.—The alkaline solution is now prepared with ease. Let fall 50° of the acid into a vessel, then make a mixture of equal parts of ammonia and water, fill the instrument to the 100°, and let it flow upon the acid, and mark the point at which the acid is neutralized; suppose it to be 20, then 80° have been used for that purpose; but it must be so made as that it will require 100°, therefore to every 80 parts of the solution experi-

* The capacity of the instrument from 0 to 100 is one ounce, and the length of the graduation had better be from eight to ten inches; of course this will vary with the diameter of the tube. As they are all to be of the same capacity, the graduation may be made upon the tube itself, or upon a piece of paper, and pasted on, then varnished, first with a solution of gum-arabic, and afterwards with copal varnish.

mented with add 20 parts of water. In making either of these solutions, one gallon can be made with the same ease as one ounce, and moreover, when they are once made there is never any necessity of recurring to the carbonate of lime, as the acid may now be prepared with aid of the ammonia.

Thus then 50° of acid dissolve exactly 50 grs. of pure carbonate of lime, and 100° of the ammonia neutralize 50 of the acid.

As using the same tube for both acid and alkali is attended with some inconvenience, having to wash it out after using one before introducing the other, I have used an additional tube, about the same diameter, and a little more than half as long as the calcarimeter, for the acid. It has simply three marks upon it, corresponding to 50°, 10° and 5° of the other tube.

Manner of performing the Analysis.—Being furnished with the two tubes, the two fluids, a cup or other convenient vessel, a small piece of glass rod a few inches long, a wine-glass and a piece of litmus-paper, a portion of which has been reddened by an acid, we proceed as follows:—Weigh out 50 grs. of the substance to be examined, place it in the cup and add to it about 1 oz. of water; fill the instrument last described up to the highest mark upon the stem with the *acid*; this is done by holding it between the thumb and fore-finger, having the little finger applied to the lower opening. After the acid is poured in, before withdrawing the finger, introduce the cork and place the fore-finger of the other hand upon the opening of the tube on the cork, for the purpose of preventing the liquid flowing out when the lower opening is left unprotected; after seeing that the acid stands exactly at the mark, it is allowed to flow gradually upon the substance. After all the action has ceased, stirring it towards the end to ensure this result, we fill the graduated tube with the solution of ammonia, in the same manner as we did the last, and let it fall gradually upon the mixture of acid and calcareous substance, arresting at will the progress of the flow by simply placing the finger upon the tube in the cork. This instrument should always be transferred to the left hand, and held in an inclined position. During the addition of ammonia the mixture should be well agitated with the glass rod, and occasionally tested by bringing a little of it upon the extremity of the rod in contact with the litmus-paper; and so soon as it ceases to turn this paper red, or begins to turn the red part of it blue, the experiment is completed; and we now look at what number of degrees the fluid stands in the tube, and are furnished with the per-centage of carbonate of lime contained in the calcareous substance examined*. We may be saved the trouble of testing too often, by paying attention to the strength of the reaction of the fluid upon the litmus-paper.

In most marls which have served as the subjects of my experiments more or less alumina is to be found, a part of which is dissolved by the acid, of which part a very good use can be made.

* If magnesia happens to be present, it will be estimated as lime, but this will very seldom be a cause of error, as it exists very rarely in calcareous manures, for which this instrument is particularly intended.

While adding the ammonia, the alumina immediately around where the ammonia falls is thrown out of solution, and if we stir the liquid the alumina will be redissolved so long as there is any free acid; so that when the flocks of alumina are no longer taken up, we are furnished with an assurance that the process is nearly completed. The acid that the alumina and iron take up is acted upon by the ammonia with almost the same readiness as if free, so that no cause of error is to be apprehended from that source.

It may sometimes happen from oversight that too much ammonia is added; notwithstanding this the analysis need not be lost. Still holding the instrument in the left-hand over the cup, having of course arrested the flow of the fluid, we pour some of the acid solution into the wine-glass, introduce the small end of the acid instrument into it, allow it to rise on the inside to either of the small marks, add this acid to the liquid, go on as before with the experiment, at the conclusion read off what is indicated, and to it add 10 or 20, according as we may have added the acid measured by the first or second mark.

After what has been said, a few words will suffice to explain how the instrument operates.

It takes 50° of acid to dissolve 50 grs. of carbonate of lime, or 1° to dissolve 1 gr., and it takes 2° of the ammonia solution to neutralize 1 gr. of the acid, and therefore in treating a substance consisting in part of carbonate of lime, for every grain that is present one degree of the acid is taken up; so that when we come to add the ammonia, we know how much of the acid is taken up by the quantity of ammonia left behind, thereby ascertaining the number of grains of carbonate of lime, which we multiply by 2 (as 50 grs. of the substance were used), to arrive at the per-centage. This multiplication is not actually performed, as the instrument is so graduated as to dispense with it.

Were it at all necessary to give any evidence of its easy application, I might state that it, along with the fluid, has been placed in the hands of persons entirely unacquainted with chemistry, and even with the principle of the instrument, and they have, with some little instruction in the manipulations necessary, obtained results only 1 or 2 per cent. out of the way in their *first* examination.—Silliman's *Journal* for October 1843.

PHARMACOLOGY.

On Madder. *By* M. Girardin, Professor of Practical Chemistry at the Municipal School of Rouen.

[Concluded from page 72.]

2. *Adulteration by Vegetable Substances.*—The vegetable substances which are introduced into the madders are powders of little or no value, such as sawdust, almond shells, bran, the bark of the so-

called pine-tree, mahogany wood, log-wood, sandal wood, and fir-tree wood.

The sophistication of madders by these different substances is much more prejudicial to the dyer than that by mineral substances; for besides diminishing, like the latter, the quantity of colouring matter of a given weight of madder, they also injure the dye, either by absorbing the colouring matter or by preventing the colours becoming so bright.

Unfortunately the means of detecting this new kind of fraud are neither so rigorous nor so simple as the process for determining the presence of mineral matters. It is extremely difficult to ascertain with what kind of vegetable substance a madder has been adulterated; it is mostly only possible to ascertain that there is a mixture. This however is the most important point, and the practical man, after all, only needs to know the tinctorial worth of the madder which he buys.

Many methods have been proposed to determine the tinctorial value of madders and the absolute qauntity of the colouring principle which they contain; but the greater part of them have the fault of being too exact, or too difficult and too long of execution. I will now point out those which I think preferable, and which I have long since employed in the examination of madders which I continually make.

One of these means consists in determining the colouring power by means of Labillardière's colorimeter; the second, in determining this colouring power, as well as the solidity and brilliancy of the colours, by an operation of dyeing. The third experiment is to ascertain the absolute quantity of the colouring principle.

These different experiments are always made comparatively, by taking for type a madder prepared with all possible care, and having the same marks as that under examination. As with indigo and other tinctorial substances, a single experiment is not sufficient; and by reason of the difficulty there is of correctly verifying the value or the quality of the madders, it is indispensable, in order to decide with any certainty, to check the experiments by each other. This is the only way of obtaining satisfactory results.

1. *Determination of the colouring Power by the Colorimeter.*—The following is the mode of operation with the colorimeter of Labillardière. The type madder and the madder under examination are dried at 262° Fahr., and an account is kept of the respective quantities of hygrometric water they contain.

25 grms. of each sample are then mixed with 250 grms. of water at 68°. After three hours of contact, the whole is thrown upon a linen cloth. A second maceration is made with the same amount of water and for the same length of time. The madders are then washed with 250 grms. of cold water, dried at 212°, and weighed, in order to ascertain the proportions of soluble, saccharine and mucilaginous matters which they have lost by these preliminary washings, which only remove an insignificant quantity of red colouring matter.

5 grms. of each of the two madders are then introduced into little

glass globes with 40 parts of water and 6 parts of very pure alum, boiled for a quarter of an hour, and the boiling liquids filtered. The grounds are washed with 2 parts of hot water. Two other decoctions, similar to the first, are made, and each time the residue is washed with 2 parts of hot water. The products of the three decoctions are combined, and the liquids from the two samples of madder compared by the colorimeter.

Without doubt this examination with the colorimeter is not sufficiently accurate, but it affords valuable indications, which, joined to those resulting from the following tests, enable us to give a decided opinion.

2. *Determination of the Tinctorial Power by Dyeing.*—In order to estimate the value of a madder by dyeing, a madder of superior quality must be taken, as a type of comparison, with which skeins or mordanted calicoes have been already dyed, by acting with determinate quantities of powder, tissue and water. Patterns for comparison should be prepared in the following manner:—

Calicoes are selected, mordanted for red and black, and well-cleansed in a dung-bath. They are divided into pieces 5 centimetres square, and are dyed with proportions of madder increasing progressively from 1 grm. up to 10 grms., so as to have a scale of 10 shades, of which the gradations represent each a known weight of madder. The garancing of these pieces is practised in the following manner:—In a great copper basin, with a flat bottom, which is covered with a layer of hay, are placed three or four glass jars with wide mouths, containing from $1\frac{1}{2}$ litre to 2 litres. The basin is filled with ordinary water heated to 104°, then into each of the glass jars the piece of mordanted calico is introduced, the madder weighed with care, and lastly, three-fourths of a litre of distilled water, heated to a temperature of 104°. A thermometer is inserted in the water-bath, which is heated slow enough for the water not to reach 167° until after an hour and a half, avoiding carefully alternations of temperature. After this it is made to boil for half an hour, the samples are taken out, rinsed in cold water and dried. Each dyed piece is cut in half; one-half is preserved as it is, the other is subjected to the following clearings:—We begin by a soap-bath at 122°, made with $2\frac{1}{2}$ grms. of white soap to each litre of water. After it has been half an hour in this bath, the cloth is carefully rinsed in cold water. A fresh soap-bath is given, to which is added half a gramme of salt of tin, and which is kept at boiling point for half an hour. It is washed and rinsed. The well-rinsed samples are dried with care and preserved from the light.

When a series of tints of two different states have been thus prepared, that is to say, a dye without and with clearing, it is very easy to ascertain the comparative value of an unknown madder. In fact, it is sufficient to take 10 grms. from the barrels, and to go through the preceding operations on 5 square centimetres of suitably-mordanted calico, and to compare the dye obtained, before and after the clearing, with the ten samples. If, for example, the shade is equivalent to No. 5 of the madder, it may be concluded that the unknown

madder is inferior by half to the madder-type, since $10 : 5 :: 100 : x = 50$.

Whatever vegetable powders may have been fraudulently introduced into the madders, whether tinctorial or inert, they can never lead to error as to the true tinctorial value of the mixture, inasmuch as the colours which they afford, and which saturate the mordants at the same time as the red principle of the madder, cannot withstand the action of the clearings as the latter does; they *run*, as is said, in the soap and tin-baths, and in the end there only remains the colour from the madder upon the tissue. The clearings are therefore necessary to show the solidity and vivacity of the tints obtained.

Instead of printed calicoes, skeins of oiled and mordanted cotton may be used in the state in which they are prepared for dyeing Turkey-red. In this case skeins of the weight of 10 grms. are taken, and dyed with different weights of good madder, from 20 to 30 grms., in order to obtain a scale of ten distinct shades.

This test is that which I have employed since 1831, and which has been since adopted in all our print-works of Rouen and Bolbec, where my pupils have introduced it. It differs very little from that which was published in 1835 by M. H. Schlumberger of Mulhausen*.

3. *Determination of the Quantity of the colouring Principle.*—The most exact process hitherto published is without doubt that made known by M. H. Schlumberger in 1838†, as modified by M. Scheurer‡. But this process, which is founded on the solubility of the red colouring principle of the madder in weak acetic acid, a fact pointed out as early as 1829 by an anonymous chemist§, is unfortunately too sensitive, and requires too great a degree of skill in the manipulation to become general.

The following is the method which I have long been accustomed to employ:—50 grms. of madder are diluted with 50 grms. of concentrated sulphuric acid. The whole is left in contact for some hours; too high a temperature should be avoided; the charcoal obtained is mixed with water and thrown upon a filter; it is then washed until the water passes through quite insipid; and next dried at a temperature of 212° Fahr. in Gay-Lussac's water-bath. This charcoal is reduced to a fine powder and macerated for two hours at three distinct intervals with cold alcohol containing a little æther, in order to free it from a fatty matter which it retains. The powder is boiled in alcohol of 0·834, at three different intervals, employing each time about 250 grms. of alcohol. When this is no longer coloured by ebullition, the alcoholic liquors are mixed, and distilled in a small glass retort to the consistence of a syrup, and the concentration of the liquid completed in the water-bath in a weighed porcelain crucible. When the extract is perfectly dry, its weight is taken. This represents the proportion of red tinctorial principle contained in the madder.

* Bulletin de la Société Industrielle de Mulhausen, viii. p. 300.
† Id., xi. p. 323. ‡ Id., xi. p. 339. § Id., ii. p. 407.

This process is rather long; it does not give, especially on a small scale, the absolute proportion of colouring principle contained in the madder; there is a slight loss, but by acting comparatively a sufficient approximation is obtained.

Such are the different methods for ascertaining the quality, the purity, or the adulteration of the madders. In most cases calcination is sufficient, and rigorously, calcination and the test by dyeing made conjointly, allow the practitioner to form a positive opinion of the value of the madders submitted to examination.

Considering the minutiæ and the number of operations which it is necessary to have recourse to, in order to form a just estimate of the relative worth of the madders, it is evident that an examination of the madders by simply looking at them, as is customary with the merchants, can afford no precise information, and must indeed lead in most cases to erroneous conclusions. The process in use amongst merchants consists in spreading samples of madders of about 30 to 40 grammes side by side on a sheet of paper, which small heaps are flattened and their surfaces rendered smooth with the back of an ivory spatula. The samples are then placed in a cellar, or some moist situation, where they remain from twelve to fifteen hours. At the expiration of this time the quality is judged of according to the brightness and tint of the powder.

But as M. H. Schlumberger* has already observed, this method does not even approximatively show the richness of colour of the madders, since a somewhat long contact with the air is sufficient to render them darker, and many circumstances may change their tint, without thereby causing their tinctorial value to vary. On the other hand, the old madders, of a dull tint, may be far superior to others of a more beautiful colour. The merchants and brokers' method of trial often places the manufacturer in a false position, by obliging him to brighten the tint of his powders, in order to make them more saleable, and that sometimes to the injury of the tinctorial power; thus facilitating the adulteration of the madders by mixture with foreign substances, suitably coloured and pulverized, which serve to heighten the tint of the powder; and it is impossible to ascertain the presence of these mixtures by exposure in the cellar, of which I have often had proofs. I have purposely made mixtures of madder, of powders of mahogany and of sandal wood in known proportions, and these mixtures, when tried by the merchants, who thought themselves very skilful in their estimation of madders, by the above process, were considered by them to be pure madders of first quality!

Testing of the Garancines.—The quality of the garancines varies, as I have already stated, considerably. A manufacturer sometimes sends a series of from fifteen to twenty barrels of excellent quality, and fifteen days later sends another series which is worth from 20 to 25 per cent. less than the preceding one. It often happens that in the same series good and bad garancine is found; each barrel therefore of this product should be tested comparatively as far as

* Bulletin de la Société Industrielle de Mulhausen, xi. p. 313.

possible. It is now customary for the seller to take back the garancines which he had delivered to the calico-printer, allowing for the pieces spoiled, when the quality of the powders was inferior to what it was represented.

The testing of garancines is made on a large and on a small scale. In the latter case the following is the process we adopt:—

Samples are taken from the barrels as they arrive, taking care to cork the labelled bottles in which they are inclosed as quickly as possible, in order that they may not dry, which in summer time especially causes an amelioration of from 5 to 6 per cent. in a few days, on account of the water which evaporates.

A piece of calico, printed in stripes of red, violet, puce and garnet, is taken (black is useless, as all the garancines produce that well), not gummed as usual, and dried. As many decimetres are cut from it as there are garancines to be tried, and the pieces are marked by notching them with the scissors: the notches must correspond with the numbers on the bottles.

From 1·9 grm. to 2 grms. of garancine, known to be good, is weighed off to serve as standard, and for the garancines to be tried, we take 1, 2, 3, 4, 5, 6, 7, 8, 10 times more or less of 1·90 or 2 grammes, according as they cost 1, 2, 3, 4, &c. more or less than the standard sample. As the samples are weighed, they are each put into a jug with a wide mouth holding half a litre, with from 2 to $2\frac{1}{2}$ decilitres of water containing some oxalic acid, in the proportion of 15 centigrms. to a litre. The jugs are numbered so as to correspond with the samples of the garancines and strips of calico. They are placed in a water-bath, in a copper boiler with a flat bottom, the pieces of printed calico are immersed in them, and dyed as in testing the madders, regulating the fire so as to raise the temperature to 158° in an hour and a half, and keeping it at the boiling-point for half an hour. After the process of dyeing, the samples are removed as quickly as possible from the vessels, rinsed in water and beaten, and then dried or previously immersed for five or six minutes in a bran-bath at 167°. When dry they are compared, and in this manner the relative tinctorial value of the garancines may be estimated as nearly as possible.

In employing calicoes, which present at the same time stripes mordanted for red, violet, puce and garnet, it is seen at once whether the garancines can be employed with advantage for all the colours, or for what tints they are most suited. I have already stated that the same garancine does not always suit equally well for red, puce and violet.—*Journ. de Pharm.* for Nov. and Dec. 1843.

Analysis of the Root of Smilax China.

According to Reinsch there may be extracted from 1000 parts of this root by æther 3 parts of a waxy substance, 4 of a balsamic resin soluble in alcohol; by alcohol of 0·876 spec. grav., 28 parts smilacine (also sugar, tannic acid, a resinous colouring substance, and a few salts); by alcohol of 0·957 spec. grav., 0·957 parts tannic acid, with salts, a reddish-brown colouring substance, and a

crystalline body; by cold water, 26 parts gum, vegetable gelatine, and salts of potash, lime and manganese; by hot water, 235 parts starch; by caustic potash, 340 parts starch, with tannic acid; lastly, 200 parts vegetable fibre and 120 water. The admission of a crystalline substance in the alcoholic extract is founded on the formation of a crystalline pellicle during the evaporation of this extract. The aqueous solution contains, besides the ordinary starch which is exclusively present in the cold aqueous and alkaline extracts, also a kind of starch, which is coloured reddish-brown by tincture of iodine.—Buchn. *Repert.*, xxxii. 145.

CHEMICAL PREPARATIONS.

On the Preparation of Osmium and Iridium. By M. E. D. Fremy.

Iridium prepared by the process of M. Berzelius has never been completely separated from osmium, for this celebrated chemist states that on heating the iridium exposed to the air it always disengaged vapours of osmic acid. The iridium which I prepare according to the following process is pure and contains no osmium. I mix first 100 grms. of the residue of platinum workings with 300 grms. of nitre, introduce the mixture into a large crucible, and keep it for an hour at a red heat in a wind furnace. After this calcination the mass is poured out on a metallic plate, which operation should be performed in the open air, and it is even indispensable to cover the face, for without this precaution the vapours of osmic acid would act violently on the skin. During the calcination with nitre a certain quantity of osmic acid is lost, but I have found that the proportion of this acid which might be condensed would never repay the inconveniences of calcining in a porcelain crucible. The decanted mass which contains the osmiate and iridiate of potash is treated in a retort with nitric acid, which liberates the osmic acid which is condensed in a concentrated solution of potash. The residue is treated with water, which removes the nitre, and it is then acted upon with hydrochloric acid which dissolves the oxide of iridium. In this manner the osmium is obtained in the state of osmiate of potash, and the iridium in that of soluble chloride.

I have found that the osmiate of potash might easily be converted into a red salt by giving off oxygen or by imparting it to other bodies. This salt, which crystallizes in beautiful octahedrons, I have named *osmite of potash*, for it contains an acid less oxygenized than osmic acid, decomposing under the influence of weak acids into osmic acid and into black deutoxide of osmium. I usually prepare the osmite of potash by pouring a small quantity of alcohol into the solution of the osmiate; the liquid becomes heated, acquires a red tint, and deposits a crystalline powder of osmite of potash; in this case the osmium is frequently precipitated entirely from solution. The salt may be washed with alcohol, which does not

dissolve it, and it then preserves without alteration. All the compounds of osmium may be prepared from it.

On treating it with a cold solution of sal-ammoniac, it dissolves at first and is then decomposed, giving rise to a new yellow salt scarcely soluble in cold water. This salt, which is so easily prepared, affords on calcination in a current of hydrogen perfectly pure osmium.

The osmiate of potash, treated with hydrochloric acid, disengages osmic acid and gives a chloride of osmium, which under the influence of sal-ammoniac forms a minimum-red precipitate very slightly soluble in water. This red salt may be employed to prepare osmium, as it affords this metal pure by calcination. We shall moreover meet with it again in the preparation of iridium.

To extract iridium I treat the chloride of iridium, the preparation of which I have described above, with sal-ammoniac; a reddish-brown precipitate is formed, consisting of a combination of the bichlorides of osmium and iridium with the sal-ammoniac.

I have fortunately found a very simple process for separating these two double salts. Sulphurous acid, by removing chlorine from the double salt of iridium, renders it very soluble in water, while the double salt of osmium undergoes no reduction. I therefore pass a current of sulphurous acid into the water in which the two double salts are suspended; the iridium dissolves, the osmium is precipitated in the state of red salt. Thus the separation of these two metals is rendered perfectly simple by the process now described.

The soluble salt of iridium crystallizes in large brown prisms in solutions of sal-ammoniac, it is therefore easy to purify it. When calcined in a current of hydrogen it affords pure irridium, which preserves in this case the crystalline form of the double salt. The soluble salt is reconverted into the black insoluble salt under the influence of chlorine.—*Comptes Rendus*, Jan. 22, 1844.

Reduction of Mercurial Compounds by Organic Substances.

From some experiments instituted by Dr. Riegel, it appears that yeast, and other bodies in the act of fermentation, are capable of causing a decomposition (reduction) of mercurial compounds, thus confirming the experiments of Schacht and Wackenroder.—*Jahrb. für Prakt. Pharm.*, vol. vii.

Employment of Electricity in cases of poisoning with Strychnine.

M. Duclos has instituted a remarkable series of experiments on rabbits, dogs and guinea-pigs. He poisoned these animals with strychnine and brucine, and then electrified them; and found that, on application of the negative electricity excited by means of an electrical machine, the symptoms of poisoning subsided, and the animals were saved; the positive electricity, on the contrary, increased the muscular contraction produced by the poison, and hastened death.

Animals which had been poisoned with arsenious acid could not only not be saved by electrifying them, but were, on the contrary,

killed sooner, whether positive or negative electricity was employed. —Buchner's *Rep. für die Pharm.*, vol: xxxii.

Efficacy of Tannic Acid in Poisoning by Hemlock.

Hitherto tannic acid, or the decoction of galls, or of any astringent vegetable, has been considered of great service in cases of poisoning by strychnine and brucine. M. Meyer had recently occasion to observe the great efficacy of tannic acid also in a case of poisoning by hemlock. Four children had eaten a large root of the water hemlock, *Cicuta virosa*, L. One child died almost immediately; to the other three sulphate of zinc was first administered in large doses to produce vomiting, which was assisted by draughts and frictions to the stomach, after which cold applications to the head, horse radish and mustard plasters were used, clysters of vinegar administered, the cold extremities rubbed with flannel and warmed, upon which a decoction of gall was administered in frequent doses and with the greatest success, for the alarming symptoms gradually disappeared, and the three children were perfectly restored after five days.—Buchner's *Rep. für die Pharm.*, vol. xxxii. 1843.

Pilulæ Ferruginosæ Valletii.

Pure sulphate of the protoxide of iron, perfectly free from peroxide and pure carbonate of soda, are dissolved separately in syrup that has been boiled, and the solutions mixed in a well-stoppered bottle, which is entirely filled by the liquid. The precipitate of protocarbonate of iron which forms is washed with boiled syrup until perfectly pure, separated from the liquid by means of a linen strainer which has been impregnated with syrup, conveyed immediately into warm honey, and the mixture evaporated to a certain weight in the water-bath. The proportions are selected so that the somewhat soft pill-mass obtained shall consist one-half of pure protocarbonate of iron. The sugar and honey preserve the preparation against any change arising from higher oxidation; the mass dissolves readily in the most dilute acids with effervescence, and the solution exhibits on testing but a very small amount of oxide. 10 grs. of the pill-mass gave on analysis 3·4 grs. of peroxide of iron, which corresponds to 5 grs. of the protocarbonate. The best form for the exhibition of this new preparation is perhaps—

Mass. pilular. ferruginos. Vallet., ʒj.
Pulveris cujuslibet, q. s. (gr. x.–xv.).
M. F. Pilul., No. 30.

Each pill contains 1 gr. of protocarbonate of iron.

1 gr. of the protocarbonate of iron, or Vallet's pills, corresponds with respect to its amount of metallic iron to—

$1\frac{6}{10}$ gr. Ferrum oxydat. fuscum.
$2\frac{1}{4}$ gr. Ferri sulphas. cryst.
$1\frac{1}{10}$ gr. Ferrum muriat. oxydulat. et
13 drops Tinct. Ferri muriatici.

The following recipe is proposed for the liquid form:—

℞ Massæ pilul. ferrug. Vallet., ʒss.
Solve in Aq. destill., ʒjj. Et adde
Syrup. (cujuslibet), ʒiiss.
Ut fiat tinctus. To be well shaken.

One teaspoonful contains one grain of the protocarbonate of iron.

Arch. des Pharm. for December.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Extract of Hops and Oil of Hops for the Preparation of Beer.

Prof. Redtenbacher draws attention to the fact, that of the constituents of the hop, the bitter substance (lupuline), the astringent substance, and the aromatic oil of hop, are the only substances which enter into the composition of beer. The aqueous extract of hop, prepared by boiling, may easily be preserved, and 12 lbs. of it correspond to 1 cwt. of hops; it contains the first two constituents. The oil of hops, which in the usual method of employing the hop is volatilized for the greater part, may be obtained by distillation with water; 1 cwt. of hops would afford 3 oz. If, then, in brewing, extract were to be employed instead of the hops, and the oil added when the beer is filled into the fermenting vats, the brewer would save all the expense of store-room for hops, avoid all the risks of the hop trade, could not easily be cheated, would be able to determine with greater certainty the quantities necessary to be added, and would require less hops, from the saving effected in the quantity of oil. The expense of obtaining the extract and oil from 1 cwt. of hops would not amount to any great deal, and by this a fourth of the hops would be saved on account of the oil; so that when the price of hops stood at 120 florins per cwt. there would be a clear saving of 25 florins on the hops alone. A butt of beer would require about 2 oz. of extract and 11 grs. of oil.—*Polytech. Central Blatt*, 1843, No. 13.

[Another advantage of this extract, should it be found to answer, would be that the English brewer might import extract from America, from which country it is impossible to import hops, owing to their bulk.—Ed. *Chem. Gaz.*]

Preparation of the Red Iodide of Mercury (Iodine Red) as a Paint.

M. Heller recommends the following method for obtaining a good iodine red. Commercial crystallized iodide of mercury is pounded and dissolved in a boiling solution of sal-ammoniac (1 part of sal-ammoniac to 1½ water). The iodide of mercury is conveyed into the boiling solution as long as any dissolves; the hot solution is then decanted and allowed to cool, upon which the iodide of mercury again separates. It is deposited in very beautiful purple-red crystals on the sides of the glass. Frequently these crystals appear at first of a pale yellow, owing to the dimorphism of this salt;

but soon after the cooling of the liquid they become as beautifully red as those which directly separate of this colour. If the solution of sal-ammoniac was too concentrated, the sal-ammoniac is frequently deposited in white crystals along with the red ones; this does no harm, as they may easily be separated by washing with water, in which they dissolve, while the latter are insoluble. When the cold liquid has been allowed to stand for half a day, the separation of crystals has terminated; the liquid is then poured off, the crystals are washed, separated by means of a glass rod from the sides of the vessel, and dried. They are not pulverized, but are preserved whole, and whenever wanted for use a small quantity is ground up with gum or oil. The colour of the crystals is not so yellowish-red as the commercial powder, the well-known iodine-red, but more of a purple-violet. The bright red colour is acquired when the crystals are reduced to powder; it is the brighter, *i. e.* has a less violet tint, the finer it is pulverized.—*Polytech. Central Blatt*, 1843, No. 16.

Adulteration of the Neutral Chromate of Potash.

According to the observation of C. Erdmann of Leipsic, there occurs at present in commerce a chromate of potash of English manufacture, which is nothing less than chromate of soda, sophisticated moreover with sulphate of soda. Now chromate of soda, when crystallized at a temperature below 86°, contains 53 per cent. water, while the potash salt is entirely free from water under all circumstances. The spurious chromate of potash in question has given rise to numerous complaints respecting its want of efficacy, and has proved indeed to contain a considerable amount of water. The adulteration is evidently not unintentional, and is based on the chromate of soda crystallizing with this amount of water at a low temperature, and then possessing the form of sulphate of soda. The chromate of soda is obtained at a higher temperature as free from water as the potash salt; and if the soda salt were pure, there would then be a gain in the amount of chromic acid with this substitution, from the equivalent of soda being lower.—*Pharm. Central Blatt.*, Jan. 3, 1844.

PROCEEDINGS OF SOCIETIES.

Meeting of the Royal Institution.

Friday, Jan. 26, 1844.

On Friday evening Mr. Brande gave a lecture "On Fermentation." The lecturer, after some successful experiments, showing the changes produced by chemical action, directed particular attention to the fact, that the presence of a body which could have of itself no apparent action is yet found to exercise a most decided influence. A portion of chlorate of potash was heated by an Argand lamp in a glass retort, and by the side of it was placed, in a retort of exactly the same size, exposed to exactly the same heat, some

chlorate of potash mixed with a small portion of oxide of manganese; after a few minutes the chlorate of potash mixed with the oxide of manganese was observed to be suffering decomposition, evolving large quantities of oxygen gas, while the other suffered no change. The oxide of manganese was entirely unchanged, and even oxide of copper, or any metallic oxide, could be substituted for it. Again, platinum resisted nitric acid; it could be boiled in it without change. Silver was, on the contrary, dissolved. Yet, on submitting an alloy of these two metals to the action of the acid, the platinum might be supposed still to escape action, but it was not so. The chemical action commenced in the silver extended to the platinum; both were dissolved. These results were precisely identical with fermentation; the action of neither was at the present moment known, and the application of abstruse chemical terms did not advance the knowledge. Experiments had however proved that no body, unless it contained nitrogen in its composition, could produce this result. On mixing a small quantity of balm or yeast with a solution of sugar and water, the following changes could be traced:—Sugar consisted of 3 atoms of carbon, 3 of hydrogen, 3 of oxygen; a proportion of carbon would, under the influence of the yeast, unite with oxygen, forming carbonic acid, and the remaining proportions would be so arranged as to form alcohol. In the manufacture of wine, yeast was not required, as the sugar of the grape contained this principle, yet the grapes could be dried into raisins without change; but that arose from the total imperviousness of the skin of the grape to air. Drying could be effected, for water could pass, but no air; allow even for a moment the entrance of air, and the change into vinous fermentation would inevitably result. There was a peculiarly instructive experiment of Liebig upon this point; he introduced into a vessel, holding a solution of sugar and water, a smaller one with a false bottom (covered with muslin), and he placed in the smaller one some yeast; and it was shown that the fermenting action had commenced in the smaller vessel, while in the larger, or outer one, although there was a free communication through the gauze, the action had not commenced, nor would it till the particles became sufficiently reduced to pass through the gauze. The presence of creosote or turpentine would stop the action of yeast; boiling might be regarded in the light of delaying it, for after some time the action could not be perceived. The lecturer, in conclusion, called attention to a very ingenious plan for brewing, suggested by Sir Thomas Marrable, by which the elaborate apparatus now employed was completely dispensed with. The malt and hops were boiled together, as at present; when it had cooled to about 90°, it was mixed with the yeast, and poured at once into the cask. The cask was fitted with a bent tube, connected with a basin of water, to prevent the access of air, while it allowed a free exit to the carbonic acid so formed. The cask required to be kept at a temperature of 60° or 70° for five weeks, and a very excellent beer was produced. The uppermost and the lowest strata were to be rejected as containing the impurities.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Products of the Oxidation of Proteine in the Animal Œconomy. *By* M. MULDER.

ACCORDING to M. Bouchardat, gelatine but rarely occurs in healthy fibrine, but *always* in the buffy coats and false membranes. That false membranes which form on tissues yielding gelatine must themselves contain gelatine, is quite clear from the analyses performed by Mulder in 1836, and is thus not at all remarkable; and it is moreover reasonable to suppose that a diseased production does not readily destroy all remains of the sound tissue.

The buffy coats certainly however contain *no* gelatine. The liquid obtained by boiling the washed buffy coat with three times its weight of water to half is abundantly precipitated by acetate of lead, and on filtering and neutralizing with ammonia another precipitate forms. If the decoction of the buffy coat is evaporated to dryness, the residue, when entirely freed from fat by alcohol and dried at 212° Fahr., contains C 51·48 and H 6·56; it is therefore *not* gelatine, which would afford C 50·37 and H 6·33. The same buffy coat, merely washed with cold water, extracted with alcohol and dried, contains C 52·53–52·95, H 6·9–7·04, N 15·51, differing thus in composition from fibrine.

The amount of substance dissolved by boiling with water amounted in one case (on only boiling for a quarter of an hour) to 14·2 per cent. It thus appears that the buffy coat must have an entirely distinct constitution. This is really the case.

In the buffy coat a peculiar body is contained, which is distinct from fibrine, albumen, caseine, as well as from gelatine and chondrine. The buffy coat must not therefore be confounded with fibrine, as has hitherto been done. It contains, besides fat (above 3 per cent.), adherent albumen, and a substance insoluble in water hitherto unobserved in animal bodies, the examination of which will be fully detailed below; it is this same substance which is obtained as a product of oxidation of proteine from fibrine and albumen when boiled with water with access of air. This matter exists already formed in the buffy coat.

The knowledge of that ingredient of the buffy coat which is gradually dissolved by water is very important, nor is the part which is

insoluble of less interest. According to the present state of our knowledge of the proteine compounds of the blood, there was reason to regard it as fibrine, the buffy coat being considered a compound of fibrine with the substance soluble in boiling water mentioned above. The portion insoluble in water is however different from fibrine; it resembles the substance which forms when fibrine is boiled with water for several hours.

The buffy coat was boiled with water, with access of air; this should have so altered it, that the remaining insoluble portion, endowed with the above properties only, should be formed. The analysis of the entire crust proved that the boiling had no influence, and that both the soluble as well as the insoluble portion, obtained by boiling for four hours, pre-existed before the buffy coat had been acted upon at all, except the freeing it from serum and fat by cold water and alcohol. It is sufficient at present to mention, that the buffy coat contains two ingredients which differ from fibrine. Berzelius announced, many years ago, that fibrine or albumen is partly dissolved by boiling with water. These experiments M. Mulder repeated and extended in 1836.

During the past year the experiments were repeated in the laboratory at Utrecht, to ascertain by elementary analysis the composition of fibrine which has been long boiled, and of the watery and alcoholic extracts. The ingredients of the fibrine and albumen soluble in water, Mulder considered to be long-boiled gelatine; since however the latter has been submitted to examination, and it has been shown that salts of lead do not precipitate the gelatine which has been boiled a long time, whilst the other precipitants indicate the presence both of proteine compounds as well as of gelatine, doubts originated as to whether the soluble matter of the fibrine and albumen were really gelatine. This required fresh examination. Mulder never entertained the opinion that gelatine was a compound of fibrine or albumen, but that it was a product of decomposition, and thus a distinct body.

Fibrine and albumen were used for examination. The fibrine was coagulated from ox-blood, the albumen from eggs, and well washed with boiling water. Both were boiled, the fluid poured off, washed with fresh water, &c.; the solutions were evaporated to dryness, the residue extracted with alcohol, and finally this extract evaporated. Mulder distinguished them as insoluble fibrine and albumen, portion of fibrine and albumen soluble in water, and portion of fibrine and albumen soluble in alcohol.

When fibrine or albumen of inflamed or healthy blood, of serum of the blood, or of hens' eggs, is boiled with water, after four hours boiling, principles are always obtained which are soluble in water, whilst the insoluble parts remain behind. Fresh quantities of the latter are dissolved by boiling with fresh water for 4–6 hours; the remaining insoluble portion contains less carbon, hydrogen, and nitrogen, but more oxygen, until the composition is finally constant. The portion of albumen or fibrine soluble in water, when evaporated, extracted with alcohol, and treated with cold water, is almost

entirely soluble in it, and contains likewise less carbon, hydrogen and nitrogen, but more oxygen than proteine. Finally, the substance soluble in alcohol is produced by boiling from the latter, into which it can ultimately be entirely changed, into a mixture of several peculiar extractive matters, whose examination will be given below. They are products of decomposition, and not higher oxidized states of proteine. When they are distilled, ammonia passes over, which is produced not only from fibrine, as Dumas has observed, but also from white of egg and all fibrinous, albuminous, and probably also caseous matters, which, exposed to a temperature of boiling water, become more or less changed, and all give a copious amount of ammonia on distillation.

To examine the substances soluble and insoluble in water more minutely, it was requisite to boil fibrine and albumen for different lengths of time in water, and to collect the products separately.

We shall examine first the different products produced by boiling fibrine from ox-blood, and egg-white in water. The analyses were instituted with fibrine, which had boiled for 4 and 26 hours in a Papin's digester, and with albumen which was boiled for 86, 127, and 150 hours in a retort.

Matter soluble in Water, but insoluble in Alcohol, obtained from Fibrine boiled for four hours and dried at 248° *Fahr.*:—

	I.	II.
Carbon	51·13	51·69
Hydrogen	6·48	6·64
Nitrogen		15·09

0·3695 gave 0·0115 ash*.

This body is precipitable by acetate of lead. If the precipitate is separated by filtration and the liberated acetic acid neutralized by ammonia, a fresh quantity of the compound is thrown down; if this is also separated by filtration and the body decomposed by sulphuretted hydrogen, a substance remains dissolved, which has the same composition; by evaporation it acquires the property of being completely precipitated by acetate of lead. The fibrine remaining undissolved was now again boiled with water for 22 hours, the water evaporated, and the residue extracted with alcohol. There remained a fresh and larger quantity than the first time of a body soluble in water, which possessed all the properties of the preceding.

The residue, undissolved by the last boiling, gave, after treating with alcohol and drying at 248°,—

Carbon	53·69
Hydrogen	6·90
Nitrogen	15·63

0·290 grm. gave 0·003 of ash.

Fibrine, boiled for several days in water in a Papin's digester, but otherwise treated as before, gave—

* The large amount of ash arises from some of the glass being dissolved by the boiling.

	Portion soluble in water, but not in alcohol.	Portion insoluble both in alcohol and water.
Carbon	51·84	53·72
Hydrogen	6·78	6·73
Nitrogen	15·67	14·82
	0·194 gave 0·010 ash.	0·540 gave 0·050 ash.

Albumen from White of Egg, boiled for 150 hours, and treated as above.—The aqueous solution of this substance was precipitated by acetate of lead, the precipitate washed, decomposed by sulphuretted hydrogen, and the liquid evaporated (I.). The liquor, filtered from the precipitate thrown down by acetate of lead, was saturated with ammonia, the precipitate then formed washed on a filter, decomposed by sulphuretted hydrogen, and the solution evaporated (II.).

	Portion soluble in water, not in alcohol.		Portion insoluble both in alcohol and water.	
	I.	II.	I.	II.
Carbon	51·38	51·99	54·99	54·55
Hydrogen	6·78	6·60	7·16	7·09
Nitrogen	15·01		15·33	
Oxygen	26·82		22·52	

If we compare the analysis of that part of the buffy coat soluble in water and insoluble in alcohol with the above obtained from fibrine after four hours' boiling, or heated in a Papin's digester, as well as from long-boiled albumen, we find a perfect accordance. They can all be expressed by the following formula:—

	Equivalents.	Calculated in 100 parts.
Carbon	40	51·45
Hydrogen	32	6·72
Nitrogen	5	14·92
Oxygen	16	20·93

This is the composition of the tritoxide of proteine, obtained when a solution of albumen, caseine or fibrine is treated with chlorine. It then forms a flocculent precipitate, whose formula is $C^{40}\,H^{31}\,N^{5}\,O^{12} + Cl\,O^{3}$. When ammonia is added to this, the solution evaporated, and extracted with alcohol, sal-ammoniac becomes dissolved, whilst $C^{40}\,H^{31}\,N^{5}\,O^{15} + HO$ remains.

Mulder calls this tritoxide of proteine, without however signifying anything more than that it contains 3 atoms more oxygen than proteine. Proteine is a very complex body; one of its constituents only probably becomes oxidized; but the newly-formed compound remains in union with the other constituents. In whatever way we procure it, from chlorite of proteine, from the buffy coat by boiling, or the decomposition of fibrine and albumen by boiling, it always possesses the same properties. In combination with metallic oxides it especially forms double salts, which are composed according to the formula $(C^{40}\,H^{31}\,N^{5}\,O^{15} + MO) + (C^{40}\,H^{31}\,N^{5}\,O^{15} + HO)$. A similar combination is also formed by the body obtained by boiling fibrine or albumen with water; it is however not possible to free the latter from dissolved glass.

The properties of the tritoxide of proteine, as obtained from chlorite of proteine by ammonia, are the same as those of the same compound obtained from the buffy coat by boiling fibrine or albumen in water; it is soluble in cold water *, but not in æther, alcohol, essential or fat oils; it has neither an acid nor alkaline reaction.

It is always precipitated in the same manner from the more or less concentrated aqueous solution, by diluted nitric, sulphuric, muriatic, neutral and basic phosphoric and tannic acid, solution of chlorine, bichloride of mercury, neutral and basic acetate of lead. The solution of the tritoxide of proteine obtained from chlorite of proteine is generally somewhat more copiously precipitated by the above agents. In saturating the acetic acid, which becomes free on precipitation with ammonia, the whole is precipitated, so that when too much ammonia has not been added, no organic matter remains in the liquid; the solution is moreover precipitated by nitrate of silver, sulphate of zinc and peroxide of iron. It is not precipitated by dilute acetic acid, neutral salts of iron and potash, ferrocyanide of potassium, which is such a delicate test for proteine, nor by chloride of barium and sal-ammoniac.

Tritoxide of proteine is gradually dissolved by potash, soda and ammonia; if the latter solution is freed from any excess of ammonia, we obtain a neutral ammoniacal salt, which enters into combination with neutral salts of metallic oxides. Of these, such as were obtained by tritoxide of proteine from chlorite of proteine were most accurately examined. With the tritoxide of proteine procured by boiling, Mulder has not prepared any salts, as it cannot be obtained sufficiently pure. The substance which remains undissolved when fibrine or albumen is boiled with water, produces on again boiling it a fresh quantity of the substance soluble in water. The undissolved residue differs from fibrine and albumen, which deserves notice because it explains an error of M. Dumas; for, on boiling fibrine, a mixture of fibrine with an insoluble substance is obtained at first, the quantity of which continually increases as the boiling is prolonged, whilst that of the fibrine diminishes; and finally a matter of uniform composition, which is represented by the following formula:—C^{40}, 53·36; H^{31}, 6·75; N^{5}, 15·45, 0·14, 24·44.

Dr. O. Laer obtained from the hair a compound of a similar composition, to which Scheerer first drew attention. It has been called binoxide of proteine. The same substance, with 14 atoms of oxygen, is obtained in an entirely different way by boiling fibrine in water. It is this which is first formed from proteine by the influence of the oxygen of the atmosphere.

The above-mentioned substance, soluble in water, originates from it by the addition of another equivalent of oxygen. Dumas has probably analysed it instead of fibrine; it contains less nitrogen, carbon and hydrogen. In this point of view albumen is entirely different from fibrine. When boiled, it is not first transformed into

* That obtained from chlorite of proteine is, after long drying, of more difficult solution in water, and is somewhat coloured.

binoxide, but directly into tritoxide of proteine. That which remains undissolved is unaltered albumen.

Nothing is now more natural than to suppose that this binoxide of proteine exists also in the buffy coat, for we there find the tritoxide of proteine abundant. The results of the analysis also show that the buffy coat is a compound of binoxide and tritoxide of proteine. We have now to ascertain if tritoxide of proteine really exists in greater or lesser quantity in the fibrine. Recollecting the somewhat less quantity of nitrogen and carbon which Mulder found in the earlier analysis, this is not improbable; it is however difficult to establish by elementary analysis, as his oxy-proteine approaches very near to proteine in composition. The property of fibrine, observed by Scheerer, of absorbing oxygen when in a moist state, gives this supposition considerable support. The fibrine must, in consequence of this property, become richer in oxygen, the longer it is exposed to the air in a moist state after its production.

According to another observation of Bouchardat, very dilute muriatic acid possesses the property of dissolving fibrine, but not coagulated albumen. This observation has been confirmed by M. Baumhauer. The fibrine is dissolved, but a small residue however, according to Bouchardat, remains insoluble, which he very improperly calls epidermose, whilst he called the dissolved portion albuminose. Other diluted acids behave like the muriatic, but they act more slowly; gluten of wheat undergoes the same change as fibrine, according to Bouchardat. But he did not observe epidermose there. Albumen from eggs and serum, as also caseine, likewise yield with muriatic acid, according to Bouchardat, a solution of albuminose. These facts deserve a more close examination, especially as Bouchardat announces that all solutions of fibrine, gluten, albumen and caseine in weak muriatic acid behave in exactly the same manner towards reagents, and must therefore contain the same substance. There is every reason to believe that the epidermose is binoxide of proteine. This substance is only contained in small quantity in fibrine, whilst almost as much albuminose is obtained as the quantity of fibrine taken. If it were so, if the fibrine contained binoxide of proteine, even in but very small quantity, this would be of importance in explaining several vital phænomena. It has not yet been possible to collect sufficient albuminose for analysis, from any quantity of fibrine made use of.

The properties of this matter agree entirely with those of binoxide of proteine. It is entirely different from the epidermis, so that the name epidermose cannot be retained. The albuminose of fibrine, or that portion soluble in muriatic acid, precipitated by carbonate of ammonia, treated with alcohol, gave on analysis by M. Baumhauer—

	I.	II.
Carbon	53·64	53·65
Hydrogen	6·88	6·73
Nitrogen	15·88	

This albuminose is therefore likewise binoxide of proteine. It is

thus evident that we cannot perform an operation with proteine, or any of its compounds, as with fibrine, in the air, without binoxide or tritoxide of proteine being at the same time formed in greater or less quantity. Proteine precipitated by solution of potash appears to possess this property least, but fibrine most. *The matters contained and remaining dissolved in the serum of the blood*, after the fibrine, hæmatine and albumen have been separated by heat, are of the most importance. M. Mulder is now engaged in an examination of this subject, and is able provisionally to assert that tritoxide of proteine is precipitated by metallic salts from the serum of blood freed from fibrine, hæmatine and albumen.

The above analytical results may be thus arranged :—

1st. False membranes contain gelatine, arising from the serous membrane on which they are formed. The other constituents are products of the inflammation, and must have the composition of the buffy coat.

2nd. The buffy coat is a compound of 2 oxides of proteine— $C^{40} H^{31} N^5 O^{14}$ and $C^{40} H^{31} N^5 O^{15} + HO$. There is probably no true fibrine contained in it.

3rd. The buffy coat is formed from the fibrine, not the albumen of the blood.

4th. Fibrine very readily absorbs oxygen from the air, even at ordinary temperatures, and forms the above two oxides of proteine. Fibrine therefore always yields less carbon, hydrogen and nitrogen than albumen, as it cannot be prepared with exclusion of the atmosphere.

5th. The epidermose of Bouchardat is probably the first, the albuminose is certainly the second of the above oxides of proteine.

6th. Albumen forms no binoxide, but tritoxide at once, when it absorbs oxygen; it therefore constantly yields more carbon, hydrogen and nitrogen than fibrine.

7th. These products of oxidation of the proteine are obtained very slowly by boiling with water in open vessels. Tritoxide only is formed from albumen.

8th. That portion which is not dissolved after boiling the fibrine in water and alcohol is binoxide; the albumen remains here unaltered, on account of its insolubility.

9th. The principles soluble in alcohol, which were retained by boiling fibrine or albumen in water, are products of decomposition of the tritoxide of proteine; this is also the origin of the ammonia, obtained when albumen or fibrine is distilled with water.

10th. The products of oxidation of proteine occur constantly in the blood; they are formed in the lungs from fibrine, *i. e.* from that ingredient of the blood, which on its coagulation coagulate into fibrine in the form of thread and bundles. The fibrine, oxidized in the lungs, is the principal, if not the only carrier of the oxygen of the air; it is especially this substance from which the secretions are formed.

11th. In inflammatory conditions a considerably larger quantity

of oxy-proteine is contained in the body than is found in the normal healthy state.

It is thus shown, amongst other things, that we *eat* binoxide and tritoxide of proteine in boiled meat; the latter exists in extract of meat, the former forms that portion which is hard and difficultly soluble. As albumen is not thus altered like fibrine, boiled albumen is perfectly distinct from boiled meat as a means of nourishment. The process of inflammation now appears essentially as a higher process of oxidation, although in a small degree the proteine oxides are constantly formed in the blood. The fibrine is expressly the carrier of oxygen, as well as the hæmatine, and the respiration is a true process of oxidation. The large quantity of oxygen thus absorbed is thus for the first time clearly explicable. In short, the old views of inflammation and respiration, advanced without scientific foundation, are now confirmed. Everything that produces hurried breathing, great exertions, fever, cold air, &c., may produce inflammation. The consequence of the inflammation is the change of fibrine into oxy-proteine, the chief ingredient of the buffy coat and the false membranes. Venesection proves antiphlogistic by directly diminishing the oxy-proteine; increased secretion of the alimentary canal indirectly produces the same effect. In the normal organism the oxidized arterial blood passes into the organs, but in this case the unoxidized proteine passes unchanged into the venous blood; the oxy-proteine however imparts its oxygen to the substances to be separated, producing on the one hand carbonic acid, and on the other proteine. A portion of the oxy-proteine may also be applied to the formation of cellular tissue, hair, skin, &c. At any rate, this discovery of the constant presence of the products of oxidation of proteine in blood, must give rise to further important investigations.

Whether oxy-proteine likewise occurs in plants has yet to be ascertained. It is not probable that plants contain true fibrine.—*Ann. der Chem. und Pharm.*, xlvii. p. 300.

Examination of the Fruit of Hippophaë rhamnoides. *By* Prof. Santagata.

At the meeting of naturalists and physicians at Boulogne, Prof. Santagata read a treatise on the chemical analysis of the above plant, which belongs to the family *Elæagneæ*. The fruit, which consists of gold-yellow berries of about the size of a pea and of a very disagreeable acid taste, was found to contain substances soluble in alcohol, others which dissolved in æther, and some which were insoluble in both these menstrua. The portion soluble in alcohol consists principally of a fatty and of a resinous body, which are accompanied by some malate of lime, a colouring and a saccharine substance. The fatty substance, washed repeatedly with water at the ordinary temperature, has the consistence of fat, burns like other fats with the cotton wick, and on incandescent iron diffusing a dense vapour of a peculiar odour; it dissolves in sulphuric acid, and the solution is coloured permanently yellow; potash and soda form soaps with it,

but not so oxide of lead, which does not combine with it, and thus distinguishes it from all other known kinds of fat, on which account it may be considered as an imperfect wax. The resin belongs to that class which by some are termed electro-positive.

The substance soluble in æther is of a beautiful yellowish-red colour, smells almost like honey, is nearly tasteless, and like a salve to the touch, becomes liquid at 122° Fahr., and burns in the air with flame. Treated with nitric acid, it becomes at the ordinary temperature thicker and of a dark yellow; when warmed it dissolves, becomes yellow, but remains oily. If the acid is neutralized with potash or soda, it acquires its primitive condition, but is less coloured. Concentrated sulphuric acid dissolves it with a beautiful black colour, which gradually passes into blue, grass-green and greenish-yellow; by neutralization of the acid, it is in this case likewise restored to its primitive state. Caustic potash and soda form soaps with it with the assistance of heat, but not ammonia. This substance has therefore much analogy with the vegetable oils.

The fat substance soluble in alcohol, administered in a dose of 12 grs. to a dog of moderate size, prostrated after a few hours the strength of the animal in a most remarkable manner, so that it could scarcely keep upon its legs; it had the appearance of one half asleep, and the pupils were dilated and less sensitive for light, the pulse was slow and small, and slight motions were perceptible at the joints, caused by involuntary contractions of the muscles. The animal exhibited during the whole time an inclination to lie extended, or curved up with the snout under the shoulder.—Dierbach *im Jahrb. für Prakt. Pharm.*, vii. p. 249–250.

On a peculiar Acid from the Oriental Bezoar. *By* M. Lippowitz.

The fragment of bezoar examined by the author was formed of thin concentric layers, the colour of which was a dark olive-green, in bands of various shades. The stone was probably in its perfect state about fourteen lines in size, and exhibited originally a kidney-shaped form. The surface was nearly entirely polished and green. In its interior the bezoar had an ellipsoidic cavity throughout its whole length, but in the author's fragment, which constituted about a third of the entire stone, the nucleus was wanting.

A careful examination and comparison of the precipitates and a microscopical investigation, convinced the author that the bezoar above described, which is neither soluble in alcohol nor in æther, consisted of a peculiar acid, to which he has applied the name of bezoaric acid. The calculus dissolved in cold solution of caustic potash with a dirty-green colour, and disengagement of a peculiar odour resembling ambergris; the solution becomes brownish red by standing. On the addition of muriatic acid, a precipitate of a dirty-yellow colour is obtained, which consists of minute microscopic crystals, aggregated in stellate groups. If a *dilute* but *hot* solution of the bezoar in potash be taken, a precipitate is obtained on the addition of dilute hydrochloric acid, in which the crystals and groups

are considerably larger, and may be well observed under the microscope with a power of 150. They are prismatic crystals, pointed at the extremities. If, on the contrary, the potash solution is *concentrated* and *hot*, the crystals thrown down on addition of muriatic acid have a different form; they are all of them peculiarly curved, resembling the letter S.

The crystals assume the same form in *cold* solutions, according to whether they are precipitated from concentrated or dilute solutions, but then they are scarcely half the size of those thrown down from hot solutions.

The bezoar, as also the precipitates obtained from solutions, dissolve without becoming black in a sufficient quantity of concentrated sulphuric acid, forming a clear dark greenish-brown solution. It is necessary to have recourse to the assistance of heat to dissolve it. On the addition of water the dissolved bezoar separates as a precipitate, exhibiting under the microscope the second form of crystal, and possessing entirely the same characters as the precipitate thrown down from a potash solution. The peculiar forms of the precipitate, and, on the other hand, the fact of the bezoar dissolving easily in potash and soda without any change, but in ammonia with difficulty, and again, its being, like uric acid, soluble in sulphuric acid, and likewise forming easily soluble compounds with lithia, induces the author to consider it as a peculiar acid. It is wholly consumed on platinum-foil without previously melting.

It dissolves in muriatic acid with a beautiful colour, resembling that of decomposed uric acid, which solution becomes yellow on being warmed and evaporated; it may be fused with potash, and then affords a clear solution in water. The solution of bezoaric acid in alkalies is easily decomposed by the weakest acids; it is precipitated even by a solution of sal-ammoniac. It appears to contain no nitrogen, or but a very small quantity; for on being fused with potash there is no formation of vapour on holding over it a glass rod moistened with acetic acid.—Simon's *Beitrage zur Phys. und Pathol. Chem.*, i. pp. 463—467.

On Absinthic Acid. By C. Zwenger.

According to Bracconot, the *Artemisia absinthium*, L. contains a peculiar uncrystallizable deliquescent acid, the ammonia salt of which crystallizes in four-sided prisms. It has been named by him absinthic acid.

To obtain this acid pure, a solution of acetate of lead is added in excess to the decoction of the plant (stem, leaves and flowers), which produces a dirty yellow voluminous precipitate. The supernatant liquid contains lead salt in solution, it being readily soluble in free acid, on which account ammonia is added to the liquid, until it possesses but a very feeble acid reaction. The well-washed lead compound is suspended in from 3 to 4 times its volume of water, and decomposed with sulphuretted hydrogen. In this operation it is necessary that the vessel containing the lead salt should be kept

constantly at a temperature of 140° to 160°, in order that the decomposition may proceed easily and be complete. The liquid filtered from the sulphuret of lead is again precipitated by acetate of lead, and the precipitate decomposed in the same manner. The filtered solution is then evaporated to the consistence of a syrup, and the residue extracted with warm æther as long as it reacts acid. The æther is distilled off, and the residuous blackish-brown mass conveyed into water, by which an acid resin is precipitated, which after a short time adheres firmly to the sides of the vessel; this resin is the so-called Absinthine. The aqueous yellow-coloured solution affords on evaporation crystals, which can only be obtained pure with great difficulty by pressing between bibulous paper and frequent recrystallization. Since the acid is volatile, this object is best attained by submitting the residue to dry distillation; the greater portion of the empyreumatic oil, which distils over at the same time, may be separated by the addition of some water; the crystals thus obtained are more easy to purify. The author subsequently, having become better acquainted with the nature of the acid, purified it by means of nitric acid. The quantity obtained is very small; 40 lbs. of the dried plant afforded scarcely a gramme of pure acid.

Pure absinthic acid has a peculiar acid taste; it is soluble in water, alcohol and æther, and crystallizes in colourless laminæ, among which occur some prismatic needles; it sublimes without leaving any residue; the vapours excite violent coughing; it undergoes no change by the action of chlorine and nitric acid. The solutions of lead and silver salts produce white precipitates in the acid; neutralized with ammonia, perchloride of iron affords a brownish-red precipitate; chloride of barium, chloride of calcium and salts of manganese do not cause any precipitate. It was found on analysis to consist of—

	I.	II.	Atoms.			Calculated.
Carbon.....	40·650	40·591	= 4	=	303·416	40·955
Hydrogen.....	5·409	5·151	= 3	=	37·438	5·053
Oxygen.....	53·941	54·258	= 4	=	400·000	53·992
					740·854	

The formula for the silver salt is $C^4 H^2 O^3 + AgO$; that of the acid is therefore $C^4 H^2 O^3 + Aq$, and the calculated equivalent for the anhydrous acid 627·37.

The numbers found, as well as the reactions of this acid, agree so accurately with those of succinic acid, that no doubt can exist as to their identity.

The succinic acid is combined in the plant with potash. If the extract be treated direct with æther, no succinic acid is obtained; but on submitting it to dry distillation, the presence of succinic can be distinctly proved in the products of distillation; it appears therefore to be contained in the *Artemisia* in the state of bisuccinate of potash, as this salt possesses the property of abandoning a portion of its acid in an unaltered state on dry distillation.

It is not improbable that other plants besides this *Artemisia* con-

tain succinic acid, which may perhaps give some information respecting the formation of amber.

Absinthine, the chemical properties of which I am now investigating, is said by M. Mein to be white and crystalline; but if we consider his mode of crystallization, there can be no doubt that instead of absinthine he obtained succinic acid, contaminated by some of the bitter substance, which led him into this mistake.—Liebig's *Annalen* for Oct. 1843.

Action of Chlorine on the Chromate of Potash. By E. Fremy.

When neutral chromate of potash is placed in a porcelain tube which is raised to a red heat, and a current of dry chlorine passed over the salt, the chlorine is entirely absorbed, and the chromate is decomposed into chloride of potassium and oxide of chromium, which latter, when obtained in this manner, is always crystallized in large brilliant laminæ. The temperature at which the reaction is effected is not without influence on the properties of the oxide of chrome. When the tube has been raised to a brown-red heat, the oxide crystallizes in large green laminæ.

When the chlorine is passed over the salt at a bright red heat, the oxide which is deposited is always crystalline, but the crystals are no longer green and friable, as in the first case, but are brown, very hard, and resemble those which are produced when bichromate of the perchloride of chromium is passed into a porcelain tube at a red heat, according to the ingenious process of M. Wöhler.

It is possible that the crystallization of the oxide of chromium under the above circumstance is due to the presence of some chloride of potassium. This crystallization resembles in every respect that of the peroxide of iron, produced by calcining sulphate of iron with common salt. The presence of a fusible salt appears to be favourable to the crystallization of metallic oxides. A large number of processes are known for preparing crystallized oxide of chrome; I believe that which I have pointed out is as quick as any other, and that it affords larger crystals.

When a mixture of chromate of potash and of charcoal is submitted to the action of chlorine under the influence of a high temperature, anhydrous chloride is then obtained, which volatilizes, and in the porcelain tube there remains a crystalline rose-coloured salt, which is a double chloride of chromium and of potassium. This salt is very deliquescent; it decomposes in water into chloride of potassium and into protochloride of chromium. The production of this double salt is somewhat remarkable, for this compound is probably formed only under this circumstance. It is impossible to obtain it in the moist way, from its being decomposed by water; and when a mixture of chloride of chromium and of chloride of potassium is heated, the chloride of chromium volatilizes without combining.—*Journ. de Pharm.* for Feb. 1844.

ANALYTICAL CHEMISTRY.

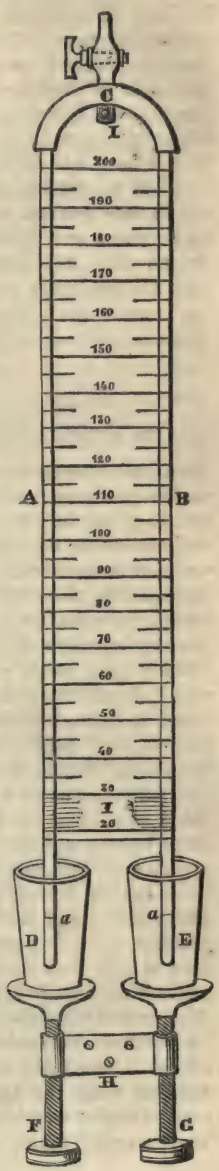
Description of an Instrument for ascertaining the Specific Gravity of Fluids. *By* F. Ham, Esq., C.E.*

Sir,—I beg to forward, for insertion in your highly popular publication, the drawing of an apparatus for readily ascertaining the specific gravity of fluids, which I devised some months since, and find extremely useful in practice.

By having the scale minutely divided, or adapting to it a vernier, it is susceptible of a high degree of accuracy, and for all ordinary fluids is infinitely superior to the gravity bottle and balance, and in many instances preferable to the common hydrometers, especially in commercial transactions, where rapidity and accuracy are essential points.

A and B are two glass tubes, from a quarter to three-eighths of an inch bore, and of any convenient length; about two feet will be found sufficient for most purposes; C a connecting brass tube and stop-cock; D and E two glasses, one for distilled water, the other for the liquid whose specific gravity is required; F and G two milled-headed screws, carrying each a stand for one of the glasses; H a bracket with two nuts, for supporting the screws and stands, F G; I I the scale, divided into 200 or 2000 equal parts or degrees.

The mode of using it is simply this:—Pour distilled water into one of the glasses, and the liquid to be tried into the other, both at 60°, or any moderate *uniform* temperature. Exhaust the air in the tubes (either by means of a syringe, or the mouth being applied at the stop-cock C) until the lightest fluid is nearly at the top of one of the tubes; then bring the surfaces of the two fluids, in the glasses D and E, on a level with the marks *a a* on the tubes, by means of the screws, raising or lowering the stands as required; the heights of the fluids in their respective tubes will immediately give their relative gravities, convertible into water at 1000, by simple proportion.



I am, Sir,
Yours very respectfully,
F. Ham.

Norwich, Jan. 9, 1844.

* Communicated by the Author.

On the Separation of Lime from Magnesia by means of Peroxide of Mercury. By M. Berzelius.

With regard to the experiments of M. Hochstetter on the behaviour of peroxide of mercury towards chloride of calcium, described at page 376, vol. i. of this Journal, from which he infers that the method proposed by Berzelius, of separating by means of peroxide of mercury lime from magnesia, is unfit for their accurate separation (Lehrb. der Chemie, 2te Aufl., x. 70), Berzelius has the following remarks:—"With regard to this I have only to observe, that it does not in the least affect the method I have given, which consists in mixing a concentrated solution of chloride of calcium, which may contain magnesia with peroxide of mercury, evaporating to dryness, and igniting the residue until all traces of mercury are driven off. A somewhat basic chloride of calcium is dissolved out, and the magnesia remains behind."—Berzelius's *Jahresbericht*, xxiii.

PHARMACOLOGY.

On an Article called Texas Sarsaparilla. By J. Carson, M.D.

Some time since there was brought to Philadelphia, and presented to the trade, an article called *Texas Sarsaparilla*. The lot in the hands of the importer was of sufficient size to render it an object to dispose of it; but the attempt, so far as we were enabled to learn, was not successful. As the article bore no resemblance to genuine sarsaparilla, the effort to substitute it for this valuable drug must have originated in great ignorance, or else in speculation of an extremely suspicious nature. From the specimen obtained at the time I shall give such a description of it as will enable it to be recognized should it again make its appearance. The packages have been made to resemble those of the genuine, about a foot and a half in length, and half a foot or more in diameter; composed of long branching stems, doubled twice or thrice upon themselves, without any attachment to a head. The lower portion of the stems is as thick as a large-sized quill, rough, wrinkled longitudinally, and of a dirty brown colour, the upper extremity thin, smooth and light brown; at irregular intervals of their length are protuberances, from which lateral branches appear to have been separated, and along the entire surface of the older and lower portions are minute fibrillæ, here and there collected in small tufts. The structure of this article is evidently *cauline*, consisting of a delicate epidermis and a thin woody layer, very tough and fibrous, inclosing medulla. The entire substance may be crushed, but cannot without difficulty be broken transversely. To powder it is impossible. It has no odour. The taste is very bitter and disagreeable. To one who is familiar with the structure of plants, it is at once evident that the article under consideration is composed of the stems of some climbing, twining plant, possessed of the habit of the *Rhus radicans*,

which has been collected and prepared in the way described, to resemble sarsaparilla. As it is stated to come from Texas, it most probably has been collected in the forests of that country.—*Amer. Journ. of Pharm.* for Jan. 1844.

On two kinds of Vegetable Wax from Brazil. By M. Sigaud.

The first kind of wax known under the name of *Carnauba*, is afforded by a palm which grows in abundance in the northern provinces of Brazil, especially in the province of Ceara. It forms a thin layer on the surface of the leaves of the tree. The cut leaves are dried in the shade; scales of a pale yellow very soon separate, which melt when heated, and give a mass of true wax, the sole fault of which is that it is rather brittle.

The first samples of this wax were sent by the governor of Rio Grande to the Count de Galveas, who in his turn sent them to Lord Grenville. Mr. Brande published an analysis in the Phil. Trans. for 1811. Mr. Brande endeavoured to discover a method of bleaching this wax, but without success. He was more fortunate in some experiments of manufacturing it into candles; his experiments were repeated at Rio Janeiro with a very satisfactory result, so that at present the substance has become an object of commerce. It meets with a ready sale in the market of Rio Janeiro, and vessels go even as far as Ceara in order to obtain cargoes of it.

The second kind of wax, known in the country by the name of Ocuba wax, is derived from a widely-distributed shrub in the province of Para, and also appears to be found in French Guiana. This shrub, which is rather bushy, scarcely attains the height of thirty hands; it grows in the marshy lands, and abounds on the shores of the Amazon river and its tributaries. It affords a fruit of the form and of the size of a bullet, containing a nut covered by a thick crimson pellicle, which imparts a red tint to water, and affords an excellent purple colour. After its first washing the nut retains its black colour; it is piled in heaps, ground and reduced to a pulp; it is then boiled for a certain time, in which operation it affords a wax, which floats on the surface of the vessel. This crude wax greatly resembles bees' wax; it has also much analogy with the wax Ibucuiba, which M. de Humboldt described on his return from America, and of which I have preserved a sample for the sake of comparison. Submitted to a process of purification, the Ocuba wax acquires a brilliant white, and is used for candles; it affords a light similar to that of gas. At Belem, the capital of Para, this wax has long been used for the manufacture of cheap candles. 16 kilogrms. of seed afford 3 kilogrms. of wax. These trees are so numerous in Para, along the banks of the Amazon river, that in the months of January, February and March the entire population is occupied in gathering the seed or fruit, as they are occupied in Europe during the months of September and October in getting in the vintage.—*Journal de Pharmacie* for Feb. 1844.

CHEMICAL PREPARATIONS.

On the Origin and Composition of Bismuth. nitr. præc. *By* L. Freundt.

Formerly the subnitrate of bismuth was prepared from a cold solution of bismuth in nitric acid; subsequently the solution was assisted by heat, and more recently Duflos has shown that the best mode of obtaining the preparation was from the neutral salt. Notwithstanding the difference in the modes of preparation, the explanation of the process remains in all the same, viz. that neutral nitrate of bismuth on its solution in water is decomposed into an acid and into a basic salt; the former of which is obtained on evaporation of the liquid in columnar crystals, while the latter formed the *Bismuth. nitr. præcip.*

To obtain the acid salt I evaporated the liquid filtered from the precipitate, in which operation a large quantity of nitric acid escaped, and dried the crystals obtained. They were intended to be dissolved in water, but to my surprise they immediately formed, just as the neutral salt on its contact with water, a basic salt, which soon subsided, while the supernatant liquid had a strong acid reaction. The latter was again evaporated, and afforded, under evolution of nitric acid, crystals, which on solution again formed a white precipitate and a supernatant liquid containing much free acid. No more crystals could be obtained on again evaporating, when the entire residue consisted of a few grains of a mass, which, on treatment with water, again afforded a white precipitate. In this manner more precipitate was obtained, on the whole, than had been employed of metal.

The neutral salt ignited afforded in 100 parts 49 oxide. 20 parts of the salt, boiled with carbonate of barytes and fresh quantities of water so long as the latter showed traces of barytes, afforded 16 parts nitrate of barytes = 6·65 nitric acid, or in 100 parts 33·25, and consequently the salt consisted of—

Oxide	49·00
Nitric acid	33·25
Water	17·75*

The salt obtained on evaporation of the liquid, treated in the same manner, afforded 49 per cent. oxide and 32·33 nitric acid.

The identity of the salts was thus proved, but it was possible that the acid salt formed was decomposed on evaporation, and under the influence of heat, into neutral salt and nitric acid. The following experiment refutes this opinion totally:—

60 parts of the crystals of the neutral salt were reduced to a fine powder, and anhydrous æther poured over them, which immediately produced a precipitate. This was washed several times with æther, and weighed 28 grms. The æther afforded, when no more odour was perceptible, 32 parts liquid, which gave off nitric acid vapours,

* In the anhydrous neutral salt the base is to the acid as 987 : 677 = 49·35 p. c. 3 atoms water would correspond to 16·8 per cent.

and after some time prismatic crystals formed in it, which on analysis proved to be the neutral salt, for it gave—

Oxide	48·30
Nitric acid	31·08
Water	20·62

A portion of the neutral salt was retained in solution by the nitric acid and by the water of crystallization of the salt, both of which had been separated by the æther from its combination with the basic salt, and on the gradual evaporation of the two liquids separated in crystals. The analyses of the three salts presents some difference, owing to the two latter not having been dried so strongly, for fear of expelling any acid which might belong to its constitution. There exists therefore no acid salt, but the neutral salt is decomposed on coming into contact with water into basic salt and free nitric acid, which latter retains in solution a portion of the neutral salt. The separation of a precipitate from acid solutions results from greater dilution, because then the acid can no longer act with sufficient energy, and loses its dissolving power.

With respect to the basic salt, Ullgren has already shown that it is not of constant composition. The amount of nitric acid and water varies according to conditions, which prevailed not merely at the formation but even at the solution of the metal. I have found in general that the amount of nitric acid is larger, the greater the relative excess of acid in the supernatant liquid, and the less the acid was saturated with metal on the solution of the bismuth. I doubt not that several subnitrates exist, such as $BiO, NO^5 + 3BiO$; $BiO, NO^5 + 2BiO + BiO, HO$; as yet however I have only succeeded in obtaining, besides the subnitrate described by Phillips, consisting of $BiO, NO^5 + 2BiO$, and that prepared by Duflos $= BiO, NO^5 + 3BiO, HO$, a precipitate in two ways, which is represented by the formula $BiO, NO^5 + BiO + 2BiO, HO$*.

When, for instance, we allow the precipitate of bismuth, prepared according to the Prussian Pharmacopœia, to remain in contact for some length of time with the supernatant liquid, then wash it with a little water, and endeavour to remove the adherent acid by careful drying, a preparation is obtained which consists of—

Oxide	80·00
Nitric acid	15·39
Water	4·61

A saturated solution, assisted by heat, and which has been rendered strongly acid by a considerable addition of nitric acid, afforded a precipitate which consisted of—

* The calculation according to this formula requires—

	Atoms.		I.
Oxide of bismuth	4	= 3948	81·40
Nitric acid	1	= 677	13·96
Water	2	= 225	4·64
		4850	100·00

Oxide	80·60
Nitric acid	14·05
Water	4·45

We may here remark that the precipitates change their composition when washed much with water. Even with the second washing the supernatant liquid does not become quite clear, supposing that the first liquid had passed almost entirely through the filter. In the next following edulcorations the precipitate separates into two parts, one of which is acid and lighter, and remains suspended for a long time in the liquid, while the heavier one immediately subsides. A quantity of the precipitate was washed about twenty times; the liquids always had an acid reaction, although this gradually decreased; the residue appeared heavier, and even changed its colour, the beautiful white passing somewhat into yellow. It contained much more oxide than originally; whether this decrease in amount of acid occurs in definite proportions or not, I have not yet ascertained.

To obtain the officinal preparation of constant composition, instead of dissolving as Duflos advises, the crystals of the neutral salt, which is not possible without a considerable addition of nitric acid, it is more advantageous to pulverize them and convey them into a known quantity of water, stirring strongly, then allowing to subside; remove the supernatant liquid as much as possible by means of a filter or by a linen strainer, and then wash once or twice with dilute alcohol.—*Pharm. Cent.-Blatt.*, Dec. 30, 1843.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Crajuru *or* Carajuru *and* Chica, *a new red tinctorial Substance from South America. By* J. J. Virey.

The leaves of various plants contain, besides the ordinary elements of vegetable organization, peculiar colouring principles; thus, for instance, blue leaves are frequently filled with indigo, as is observed in *Polygonum*, *Isatis*, *Nerium*, *Pergularia*, *Hedysarum*, *Galega*, &c., for even the cows which feed upon them sometimes give blue milk.

Other leaves naturally become red, owing to certain properties peculiar to their juices, but especially to the action of heat and light. These kinds of vegetables, generally astringent or acid, are more frequent in southern countries, where they develop their red tints to a greater extent at an advanced period of vegetation, as in autumn; this is the time for obtaining peculiar red dyes. We might enumerate a long list from among the *Rubiaceæ*, *Rosaceæ*, *Leguminaceæ*, &c., even of our temperate climate, but the richest tinctorial products are peculiar to intertropical regions.

M. de Humboldt has described in the 'Annales de Chemie et Physique' (vol. xxvii. p. 315), under the name of *Chica*, a vegetable

product of a brick-red colour, obtained by macerating in water the leaves of *Bignonia chica*, a shrub of the family of the *Bignoniaceæ* from equinoctial America.

As we have obtained from Para in Brazil, under the denomination *Crajuru* or *Carajuru*, a substance not only analogous in its physical and chemical characters to the *Chica*, but of a red brown violet tint, much more beautiful or rich, and like vermilion, whilst the other appeared duller and much inferior, it may be useful to give fresh details about this product, which has been imported to be tried in dyeing.

The *Crajuru* or *Carajuru* (*Carucuru* according to others) is a kind of powder or fecula, in pieces somewhat light, inodorous, insipid or slightly bitter, not soluble in water, but soluble in alcohol, æther and the oils and fats, without being completely resinous, burning with a flame, but leaving a quantity of gray cinders. It is wholly dissolved by alkalies, and acids precipitate it without greatly altering its colour, if they are not concentrated.

The *Chica* of M. de Humboldt came from the neighbourhood of the Orenoko, near Rio Meta; but the *Crajuru* seems to be the kind mentioned by Hancock, from Guiana, as being purer, and sent in the form of balls, enveloped in the bark of trees or palm-leaves. Indeed, the *Crajuru* is of an intense violet tint, with a coppery lustre when rubbed on a hard body. MM. Boussingault and Rivero also state that it is advantageously used in dyeing.

It would therefore appear that it is not only the *Bignonia chica*, but perhaps other kinds of shrubs of the same genus, which afford the finest *Carajuru*. The Galibis, and other savage tribes, boil the stalks and leaves of these *Bignoniæ*, which are of a red tint at their advanced period of vegetation, to obtain it. It is passed through a sieve made of the bark of a tree, and the fecula is well washed in water, and then exposed to the sun to dry.

The natives only use the *Chica* or the *Crajuru* for painting the skin, either as a defence against humidity and the bites of insects, or as a brilliant ornament, and in order to render themselves formidable in their wars. For this purpose they pound the *Chica* or *Crajuru* with a fat liquid, as the bitter and yellow oil of the fruit of the carapa (*Xylocarpus carapa*), made fragrant with the balm aracouchini (*Amyris heterophylla*, Wild). Other travellers assert that the aborigines prefer the fat of tortoises, which is green, or still better, the musky fat of the *Crocodilus acutus*, for making a kind of *Chica* pomatum, and anoint their skins with it.

The *Crajuru* now brought into Europe must furnish a rather strong and beautiful dye, the brilliancy of which appears quite superior to that of orleans*.

* The drink called *chica*, which is so much used among the people of South America, must not be confounded with the subject of the present notice. This drink, in fact, is prepared with pods of algaroba (*Mimosa algaroba*), which are nearly as sweet as the carouba of the *Ceratonia Siliqua*, and with the bitter stalks of the *Schinus molle*. It is said that old women are employed to chew these *Algarobæ* and the *Schinus*, and then to spit them into a vessel; water is added; the whole soon ferments, and affords a kind of intoxicating beer.

Receipt for Blue Sealing Wax.

M. Weyer proposes the following receipts:—

Dark Blue.—1 part shell-lac, 1 dammara resin, ½ burgundy pitch, ½ venetian turpentine, 1½ ultra-marine.

Light Blue.—Same as the above, with the addition of ½ part of dry sulphate of lead.—*Polytech. Zeitung.*

PATENT.

Patent granted to Charles Maurice Elizee Sautter, *for Improvements in the Manufacture of Borax.*

The object of the invention is to avoid the use of water in the manufacture of borax, and to produce an article thereby possessing the same properties as the crystallized borax manufactured by the usual process, but of an entirely different appearance, being in a granular state, and of a dull white colour when quite pure. The advantage of this invention is to produce an article, endowed with the same chemical properties and of precisely the same composition, at a considerably less cost than the borax now in use; it may be added, that its being in a granular state makes it more convenient for the making of glass enamel, &c. This new borax is made in the following way:—About 38 parts in weight of boracic acid, quite pure, crystallized and dry, are taken and sifted; then about 45 parts in weight of fine carbonate of soda, crystallized, reduced to a powder, added. These two powders are to be thoroughly mixed together by any convenient means. The mixture is then to be placed in a room, the temperature of which is heated to about 90° to 115° Fahr.; it is placed in layers or beds, of about one inch thick, upon wooden planks. The action of the heat upon the mixture causes the boracic acid to combine with the soda, and the carbonic acid is driven off from the carbonate of soda, together with the superabundant water contained in it, forming thereby, without the aid of water, a perfect borax, or borate of soda, possessing all the chemical properties of the borax now obtained by means of crystallization. The layers should be left during from 24 to 36 hours, being stirred now and then; after which the operation is completed, and the new borax is found in the state described ready for the market. This description applies more particularly where both substances are used in their purest state; impure acid can however be also used, and the reaction will take place just in the same way, and offer proportionally the same advantages over the actual mode of manufacturing borax by crystallization; but an impure borax will then be obtained, which, however, not being objectionable for certain purposes, might also be used.—Sealed May 22, 1843.

THE CHEMICAL GAZETTE.

No. XXXIV.—March 15, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constituents of the Lymph. *By* H. NASSE.

THE lymph which forms the subject of the following analysis was collected from the lymphatic vessels of the neck of several horses. It was dried and pulverized, and weighed, after having been dried in the water-bath at 212°, 255·5 grms. It had the appearance of dried albumen, and diffused on pulverization a peculiar disagreeable odour. It was treated five times with boiling æther, which on being removed left behind 0·45 gr. of a liquid fat, which had a strong and somewhat aromatic odour. The alcoholic extract was of a brownish colour, and weighed 7·10 grs. The powder was now digested in alcohol of 0·845 spec. grav., until this no longer became coloured, and left but a scarcely-perceptible residue on evaporation. The brown extract weighed 13·63 grs. The residue was now boiled, digested, and washed with cold water so long as this passed through turbid; at first it was yellowish, and subsequently colourless. The extract, which amounted to 32·05 grs., resembled gelatine when inspissated. It had however less odour than that prepared from hydropic fluids.

The insoluble portion of the lymph was calcined first in a porcelain crucible, and then for several hours with constant stirring in an open platinum dish, until the residue formed a fine, white, faintly-yellowish ash, which contained 1·90 gr. salts soluble in boiling water.

Each of the three extracts (with absolute alcohol, hydrated alcohol and water) was burnt separately, and then the salts soluble in water extracted, and after drying weighed in a crystalline state. The black ash from each extract was then ignited in a platinum dish, until the whole of the carbonate disappeared. In this manner it was easy to calculate how much organic substance it had contained. The proportions were—

	Extract with absolute alcohol.	With alcohol of 0·845.	Aqueous extract.
Salts soluble in water..	3·21	9·10	15·20
Insoluble residue.....	0·03	0·05	0·25
Organic substance	3·86	4·48	16·60
	7·10 grs.	13·63 grs.	32·05 grs.

Before the extract with absolute alcohol was burnt, the author endeavoured to obtain urea from it by removing the salts by frequent treatment with absolute alcohol, and careful evaporation of the solution until the mass dissolved quickly and without residue in alcohol; after evaporation water was added. The turbid solution thus obtained passed perfectly clear through the filter; it was evaporated to within a small residue, and after cooling some nitric acid added. The precipitate, which formed only in the cold and on desiccation, consisted solely of drops of fat, without any admixture of a crystalline substance, which was ascertained from examination under the microscope. There was consequently no urea contained in the aqueous solution of the alcoholic extract freed from common salt and fat, but only alkaline oleate.

To ascertain more accurately the nature of the salts contained in the lymph and the mode of their occurrence, the three portions were analysed, and were found to consist of—

	Salts from both the alcoholic extracts.	From the aqueous extract.	From the insoluble residue.
Chloride of sodium	8·781	12·170	0·115
Carbonate of soda	2·939	1·600	1·261
Phosphate of soda	0·230	0·330	0·053
Sulphate of potash		0·820	0·370
	11·950 grs.	14·920 grs.	1·799 gr.

The phosphate and carbonate of soda cannot have been extracted as such by either the absolute or weak alcohol, as they are not soluble in these media; the former has probably originated from the combustion of the phosphorus in combination with the fat and with the other organic constituents. The amount of the phosphate obtained in this manner is so inconsiderable, that it is not opposed to this view. The carbonated alkali of the alcoholic and spirituous extract was either in combination with lactic acid or with a fat acid, for instance oleic acid.

According to recent investigations, lactic acid does not occur in the blood*.; it can therefore not occur in the lymph; and since, on the addition of nitric acid to the perfectly clear aqueous solution of the alcoholic extract, a considerable turbidness resulted, arising from the separation of particles of fat, the presence of a soda soap in the lymph is satisfactorily proved.

That so much salt should be extracted by water from the dry lymph after long-continued treatment with alcohol and spirits, is not surprising, since this salt, which is somewhat difficult of solution in those liquids, was difficult to extract from the unsoftened particles of the fine powder†. It is therefore very possible that the amount

* See this Journal, p. 33 of the present volume.

† Albumen, even after long-continued boiling with water, constantly retains a portion of inclosed salt, which is larger than that retained by fibrine under the same circumstances: since the statements of chemists do not agree with respect to the amount of salt which occurs in the ashes of albumen and of fibrine, the author has made an analysis of these substances, from which he has removed as

of the three extracts with æther, alcohol and spirit, would have been somewhat higher in the examination of fresh lymph.

The insoluble residue of organic substance consisted, as earlier analyses of the lymph have shown, of albumen and some fibrine. The latter could, as is well known, no longer be separated from the former after desiccation. The salts found in this residue presented totally different proportions to those of the extract. It is remarkable that among them the carbonate alkali predominates, although it is asserted by some chemists that the ash of pure albumen affords neither carbonate nor free alkali. This carbonate or free alkali must have been in more intimate combination with the albumen than the other salts, for it is not possible to conceive how the chloride of sodium should have been extracted almost entirely by spirit and water, and the carbonated alkali remain behind to so large an amount. It is true indeed that in the burning and calcination of the albumen with salt, a portion of the chlorine is set free; but this loss of chlorine is however not so considerable as to explain the amount of carbonate of soda. The alkaline sulphate of the lymph cannot have arisen solely from the combustion of the sulphur combined with the proteine to form albumen; in the first place, because the quantity is too large in proportion to the albumen; and secondly, because the aqueous extract afforded more than as much again of the sulphate as the boiled albumen.

The ashes insoluble in water from the extracts and albumen formed too small a quantity to be submitted to accurate analysis. The quantity of iron in the ash was so extremely minute, that it could not be separated from the phosphate of lime, the weight of which did not even amount to one-tenth of a grain; the same was the case with respect to the trace of phosphate of magnesia, which adhered to the phosphate of lime. The author contented himself with precipitating by ammonia the phosphate of lime, with the traces of iron and magnesia, after separation of the silica by re-solution of the ash in hydrochloric acid, in which it had previously been dissolved. There was no subsequent separation of the precipitated constituents with acetic acid. The carbonate of lime was then obtained in the usual manner as oxalate, the carbonate of magnesia as phosphate.

The collective result of the analysis is—

much as possible the salts. Dried serum of various animals, from which the fat had been extracted with æther, was reduced to powder, and then boiled and digested with distilled water for several days. The pure washed fibrine, which was likewise derived from various kinds of domestic animals, had lain for some months in alcohol before it was dried, pulverized and boiled. 250 grs. of each substance were calcined, which was effected much more easily with the fibrine than with the albumen. From the latter the author obtained 1·175 gr., from the former 0·240 gr. soluble salts, or 0·470 per cent. and 0·096 per cent., and these consisted of—

	Albumen.	Fibrine.
Salt	0·211	0·052
Sulphates and phosphates	0·259	0·044
	0·470	0·096

Æthereal extract	0·088	
Alcoholic extract	0·755	
Spirituous extract	0·877	
Aqueous extract	3·248	
Albumen with fibrine	39·111	
Oleate of soda	0·575	
Carbonate of soda	0·560	
Phosphate of soda	0·120	5·611
Sulphate of potash	0·233	
Chloride of sodium	4·123	
Carbonate of lime	0·104	
Phosphate of lime with some iron	0·095	0·310
Carbonate of magnesia	0·044	
Silica	0·067	
Water	950·000	
	1000·000	

M. Nasse obtained a large quantity of serum from a healthy horse, from which he prepared the salts by a careful calcination in two portions, separating the aqueous extract obtained by boiling from the coagulated albumen. The relations of the various salts to each other were nearly the same in these two portions as in the lymph, with this difference only, that the albumen, from its having been less completely boiled, afforded proportionately more chloride of sodium. The carbonate of soda was likewise in this case, as in the albumen of the lymph, the most abundant salt, while in the aqueous extract there was six times as much chloride of sodium. On adding up the corresponding salts from the two portions of the serum, and reducing their proportions to each other to 5·611 (which was the number representing the amount of salts in the lymph), there was a remarkable coincidence in the composition of the two mixtures of salts, supposing the oleate alkali in the lymph had also been calculated as carbonate. This salt was not removed by alcohol from the serum previous to ignition. The numbers are as follows:—

	Serum.	Lymph.
Alkaline chloride	4·055	4·0123
Alkaline carbonate	1·150	1·135
Alkaline sulphate	0·311	0·233
Alkaline phosphate	0·115	0·120
	5·661	5·5003

The lymph therefore is a dilute serum, and the salts of the blood, which make their exit along with the colourless blood-liquid from the capillary vessels, either return in the same proportions to each other as they were secreted, again into the capillary vessels, so that the previous relation in what remained behind is not disturbed; or they penetrate, which is more probable, only into the lymphatic vessels.

Besides there being more water in the lymph than in the serum (950 to 922), the two liquids differ in the proportion of

their solid constituents to the salts, which in the first liquid is as 88·7 : 11·3, in the latter as 91·2 : 8·8. It is probably precisely this circumstance which causes the much greater viscosity of the serum, which is by no means solely dependent on the greater degree of concentration of the albuminous solution.—Simon's *Beiträge zur Phys. und Pathol.*, ch. i. pp. 449–457.

Chemical Examination of Truffles. *By* M. Riegel

The following substances, deserving of mention, occurred in Perigord truffles examined by the author:—A brown fat oil (oleine), with traces of an essential oil, a resin of an acrid irritating taste, osmazome, fungic acid, mushroom sugar, boletic acid, phosphoric acid, potash, ammonia, vegetable gelatine, vegetable albumen, pectine and fungine.

Brown fat Oil.—This oil is obtained on digesting the dried and pounded truffles with æther as long as any is removed, upon which the greater portion of the æther is distilled off, and the residue evaporated in an open vessel; a yellowish, or rather a greenish-brown oil is left, of a peculiar, rather agreeable odour of roasted apples, and of a disagreeable, somewhat rancid, acrid and irritating taste. After some time crystals of stearine separate. It reddens blue litmus-paper, sinks in water, affords on distillation a trace of a volatile oil, and dissolves in alcohol, especially when warm, and in essential oils. Caustic potash and ammonia have but a slight action on it at the ordinary temperature, but with the assistance of heat saponification results. Mixed with sulphuric acid, it dissolves in it at first to a reddish-brown liquid, becoming dark brown, and finally black, of a thick consistence; it is decomposed by water.

Brown acrid Resin is obtained when the alcoholic extract of the truffles is digested with æther to remove the brown fatty oil, the residue treated with water, which dissolves the osmazome, &c., and the residue dissolved in alcohol. The greater portion of the alcohol of the spirituous solution is removed by distillation, and the residue evaporated to dryness, at a gentle heat, in the water-bath. The resin forms a dark yellowish-brown mass, void of smell, and of an acrid irritating taste. It dissolves pretty readily in alcohol, in fat and essential oils, but with great difficulty in caustic potash, soda and ammonia. The alcoholic solution faintly reddens litmus-paper; solution of ammonia produces a considerable turbidness in it.

Alcoholic solutions of acetate of lead and nitrate of silver produce in the alcoholic solution of the resin dirty white precipitates. Concentrated sulphuric acid dissolves the resin without decomposition; the solution is thrown down by water. Nitric acid dissolves it with the assistance of heat, with evolution of nitric oxide; and if the action be continued, there is formation of artificial tannine and some oxalic acid.

Mushroom Sugar.—To prepare it, the fresh fungi are triturated with a little water, the mass strained, pressed, and the liquid evaporated nearly to dryness; the residue, or the extract obtained by

treating dried coarsely-pounded fungi, such as *Morchella* and truffles, with boiling water, is digested with alcohol as long as anything is dissolved, the greater portion of the alcohol is then removed by distillation; from the brown liquid, crystals of impure mushroom sugar are deposited, which are purified by frequent solution in boiling hot alcohol and recrystallization. This sugar exhibits a great inclination to crystallize, both from its aqueous and from its alcoholic solution; and on spontaneous evaporation it separates in long, white, shining, four-sided prisms with square base. One drop even of a dilute solution affords on drying upon glass a beautiful growth of crystals. From this great inclination to crystallize, it is easily detected in fungi, and is therefore not easily confounded with any other sugar, at the furthest only with mannite. In alcohol and water it is less easily soluble than cane-sugar, tastes less sweet than cane, grape and manna sugar, and its solution in water passes into the vinous fermentation upon the addition of yeast. It melts when gently heated, and solidifies to a clear, colourless, transparent mass, which on being exposed to a higher temperature disengages gas, becomes yellow and finally brown. Concentrated sulphuric acid dissolves it with a red colour; an addition of water causes a separation of a white coagulum. The author could not detect the vapours of æther, observed by Schrader on acting with sulphuric acid on the sugar of *Helvella Mitra*. It affords malic and oxalic acids, but not mucic acid, with nitric acid; hydrochloric acid dissolves it to a colourless liquid, from which solution it separates unchanged. Caustic solution of potash dissolves the sugar, forming a colourless liquid, but the sugar loses its sweetness in this case; it combines with the alkaline earths and with some metallic oxides. The behaviour of mushroom sugar towards bases and salts the author intends to make the subject of a separate investigation, the results of which he will publish at some future time.

Fungic Acid was obtained, according to Braconnot's method, by expressing the pounded fungi, and heating the sap to coagulate the vegetable albumen, then filtering and evaporating the liquid at a gentle heat to the consistence of a syrup. The residue, or the extract prepared by treating the dried and pounded fungi with boiling water, is digested with alcohol, which leaves undissolved the fungic acid compound, which is well washed with alcohol. The residuous brown mass is dissolved in water, filtered, and a solution of nitrate of lead is added to it as long as any precipitate is produced. The precipitate of impure fungate of lead is decomposed with ten times its weight of dilute sulphuric acid, and the fungic acid so obtained is saturated with ammonia and evaporated to crystallization. The fungate of ammonia is freed by frequent recrystallization from colouring extractive matters; and as soon as it is obtained colourless, it is dissolved in water, precipitated with acetate of lead, the well-washed precipitate decomposed either with sulphuric acid, or rather with sulphuretted hydrogen gas, and the liquid filtered from the sulphuret of lead, evaporated to the consistence of a syrup.

The great solubility of the fungate of ammonia renders its pre-

paration in a pure state, and consequently also of the pure acid, very difficult, from the extractive matters always accompanying it. M. Riegel found the following process for the preparation of the pure acid preferable :—The liquid obtained by decomposition of the impure fungate of lead with dilute sulphuric acid is saturated with carbonate of soda, the solution evaporated to dryness, and the residue of fungate of soda treated with alcohol of 0·86 spec. grav. as long as it is coloured. The residue insoluble in alcohol is dissolved in water, and the solution thrown down by acetate of lead; the precipitate of fungate of lead, which is now white, is carefully edulcorated, decomposed with sulphuretted hydrogen, and the filtered acid liquid evaporated to a syrupy consistence.

Fungic acid is a syrupy colourless liquid, without smell, and of an acid acrid taste; it absorbs water from the atmosphere, mixes with water and alcohol in every proportion, and dissolves in æther, but only in a certain proportion. It turns blue litmus-paper red, cannot be obtained crystallized, and deliquesces after having been dried; the ammonia salt crystallizes with excess of acid in large regular prisms, which dissolve in 2 parts cold water; the lime salt in small four-sided prisms, which are difficult of solution in cold water. Fungic acid precipitates acetate of lead and nitrate of silver entirely only when in combination with bases, for both these fungates are easily soluble in free acid.

Boletic Acid.—To obtain the boletic acid, the expressed juice of the fresh, or the aqueous extract of the dry fungi, is evaporated to a syrupy consistence, and treated with alcohol of 0·845 spec. grav. The undissolved residue, after having been well washed with alcohol, is dissolved in water, the solution precipitated with nitrate of lead, the edulcorated residue decomposed by sulphuretted hydrogen gas, and the dilute acid so obtained evaporated, when the boletic acid separates in small white crystals, leaving a very acid mother-ley, which along with fungic acid contains phosphoric acid. The acid is obtained pure by dissolving the crystals in alcohol and evaporating the filtered solution; it forms small colourless four-sided prismatic crystals, which resemble those of tartar, have no smell, a very acid taste, are gritty between the teeth, are not altered by exposure to the air, dissolve in 160 parts water at 68° F., and in 40 parts alcohol of 0·845 spec. grav. Boletic acid possesses the property of precipitating the peroxide of iron wholly from its salts; the protoxide, on the contrary, it does not precipitate. The boletate of the peroxide of iron is of a rusty-red colour, and is thrown down both by the free acid and by its salts.

Fungine is white, or rather yellowish-white, fibrous, soft when moist, slightly elastic, and of an insipid taste. Moistened with water and exposed to the air, it becomes softer, and enters into putrefaction, giving off at first an insipid, subsequently a rotten animal odour. The water does not act on test-paper, contains a very minute quantity of sulphuretted hydrogen, and affords with acetic acid a gelatinous precipitate. Concentrated sulphuric acid carbonizes the fungine, and nitric acid dissolves it with disengagement of nitric oxide.

At first it is coloured yellow, then softens, swells, and is converted into bitter substance, tannine, oxalic acid and prussic acid. Boiled with concentrated muriatic acid, it is converted into a gelatinous substance, which dissolves and is re-precipitated from the solution by an alkali. By boiling with dilute acid, fungine is converted into a soft semi-gelatinous substance, which becomes hard by digestion with basic acetate of lead or with infusion of galls, by the absorption of lead and tannic acid. A concentrated boiling solution of caustic potash slowly dissolves the fungine to a soapy mass, which is precipitated by acids in flakes. Fungine burns when dry without melting or swelling, with a lively flame, diffusing an odour of burnt bread, and leaving behind a white ash, containing phosphate of lime.—*Jahrb. für Prakt. Pharm.*, vii. p. 222.

Heat from solid Carbonic Acid. By W. F. Channing.

There is a remarkable reaction between solid carbonic acid and the caustic alkalies. If a small piece of solid carbonic acid be wrapped in cotton with a little pulverized caustic potash, and the whole be pressed between the fingers, so much *heat* is evolved as to make it uncomfortable to hold. This is the most remarkable illustration of heat from chemical union. One of the agents employed is the coldest substance in nature with which we are acquainted, that which we select to show the effects of extreme refrigeration. The other is at the natural temperature. Both moreover are in the dry or solid state; yet their union or simple contact produces heat sufficient at least to inflame phosphorus. This reaction is noticed, as it suggests some striking experiments. It has very possibly been observed by others, though it is not referred to in various works on the subject.—Silliman's *Journal* for Jan. 1844.

Observations on the Volatile Oil of Betula lenta, *and on Gaultherine, a Substance which by its Decomposition yields that Oil. By* William Proctor, Jun.

[The highly interesting results obtained by M. Cahours in his examination of the oil of gaultheria will be fresh in the recollection of our readers. From the researches of that chemist it was proved that this natural oil was a combination of salicylic acid with the oxide of methyle; and that by distilling a mixture of pyroxylic spirit, salicylic acid and sulphuric acid, a product was obtained having the identical properties of the volatile oil; thus exhibiting the first instance of this pyrogenous body (oxide of methyle) occurring in a natural production. (See this Journal, vol. i. pp. 365 and 535.) The present article, for the communication of which we are much indebted to the author, will be read with considerable interest, as it not only proves the existence of this remarkable oil in one of the members of a widely different tribe of the vegetable kingdom, but adds to our knowledge a new and peculiar principle, which

bears a general resemblance in its properties to that small but remarkable class of bodies, amygdaline and sinapisine.—Ed. *Chem. Gaz.*]

Oil of Betula lenta.—The plant which yields this volatile oil is one of the most noble individuals of the American forest, both as to its gigantic size and to the various œconomical uses to which its wood has been applied in cabinet work, &c. It attains the height of eighty feet, and grows abundantly in the middle and northern states and in Canada, and is known under the various titles of *sweet birch*, *black birch*, *cherry birch* and *mountain mahogany*. The bark and leaves are imbued with the odour and taste of the *Gaultheria procumbens*; and this similarity in sensible properties suggested the idea of an analogous chemical constitution of their volatile oils.

25 lbs. of the bark, taken from the trunk and larger branches, deprived of its external layers, was coarsely bruised, macerated for several days in as much water as would cover it, and then submitted to distillation. By this treatment the bark yielded 5 drms. of volatile oil, besides that portion which remained in solution in the distilled liquid. Several circumstances interfered with the success of the operation, and it is probable that the amount of oil indicated is less than it might have been under more favourable auspices.

Volatile oil of *Betula lenta*, as obtained by careful distillation, is colourless, has the specific gravity 1·173, and in odour and taste closely resembles oil of gaultheria. Like that oil, when exposed to the air, it gradually acquires a red colour, of which it is easily deprived by distillation. It is also obtained colourless by decomposing its compound with potash by a dilute acid. It is slightly soluble in water, to which it communicates taste and odour, and mixes in all proportions with alcohol and æther. Its aqueous solution is coloured purple by persulphate of iron. Dropped into a concentrated solution of potash, combination immediately ensues, with the production of a solid compound and the evolution of heat. This product, when pressed between bibulous paper to remove the excess of potash, and then dissolved in hot alcohol, is obtained in rhombic and six-sided tables by its evaporation. When one of these crystals is placed in contact with a drop of dilute sulphuric acid, it is at once decomposed, minute globules of oil float on the surface of the liquid, and the odour of the oil is developed. It reacts with caustic soda and baryta, and with oxide of lead and copper, in the same manner as the oil of gaultheria.

When heated with an excess of potash, salicylic acid is produced; and when agitated with solution of ammonia, it is gradually dissolved, the solution depositing crystals in all respects like those from the oil of gaultheria.

By passing a current of chlorine over the oil of *Betula lenta* it is rapidly absorbed, hydrochloric acid is evolved, and the oil gradually becomes a solid crystalline mass of a yellow colour. If this be dissolved in boiling strong alcohol, the solution deposits it in brilliant

four-sided plates, like the gaultheria compound, which possesses the same properties.

Bromine combines with the oil, hydrobromic acid being evolved.

By distilling the chlorine compound with iodide, cyanide, or sulphuret of potassium, compounds of the oil with iodine, cyanogen and sulphur appear to be formed. The latter condenses as a yellow oil, which by standing becomes crystallized, and has a very fetid odour.

Ordinary nitric acid (1·40 spec. grav.) has little action on the oil when cold, but by heat a rapid evolution of red fumes occurs, and the oil is converted into a crystalline matter, having acid properties. It crystallizes in minute prisms, and combines with fixed bases to form salts, which fulminate by placing them on a hot surface. Fuming nitric acid acts unassisted by heat. Both these products appear identical with the corresponding compounds of oil of gaultheria.

When oil of *Betula lenta* is mixed with concentrated sulphuric acid, but little change occurs; but if heat be applied, the oil is gradually dissolved, the mixture acquires a deep red colour, and the odour of the oil ceases to be perceptible. If now it be allowed to stand, the solution becomes a mass of crystals, which after the removal of adhering sulphuric acid have the properties of salicylic acid. By pressure between bibulous paper, and crystallizing from a hot solution in water, the acid is obtained perfectly pure and white. Oil of gaultheria yields salicylic acid under the same circumstances. If the acid be in great excess, or too much heat be applied, the operation fails. It is probable that in this reaction the acid acts on the methylic base of the oil, setting the salicylic acid at liberty. This is an interesting fact, and deserves attention.

Gaultherine.—The dry bark of the *Betula lenta* does not possess the peculiar odour of its volatile oil, which latter is only developed by the contact of water. The analogy of this fact to that of the wild cherry bark, rendered it probable that a principle existed in the bark which by its decomposition yielded the oil. When the powdered bark is treated with cold alcohol of 95 per cent. by maceration and displacement until it is exhausted, the residue of the bark no longer gives an odour of gaultheria when moistened with water. If the alcoholic liquid be evaporated to an extract, and a portion of it be mixed with a part of the exhausted bark in water, the peculiar odour of the volatile oil is immediately developed, and by distillation a liquid is obtained which is coloured purple by the persulphate of iron, and otherwise reacts like the oil of *Betula lenta*.

Gaultherine does not appear to exist in the *Gaultheria procumbens*. The leaves of that plant were dried, powdered, and treated like the bark of *Betula lenta*, but they did not yield that principle. The leaves of the Gaultheria, when long kept, lose their odour, and mixture with water does not revive it, as with *Betula lenta*; hence it would seem that the salicylate of methylene is an immediate product in the *Gaultheria procumbens*, whilst in the *Betula lenta* it is secondary.

In order to obtain this principle as pure as possible, the alcoholic extract of the bark is treated with water, which leaves the resin and fixed oil. The dark red liquid thus obtained, containing tannine, extractive and saccharine matter, is then treated with an excess of hydrated protoxide of lead until these substances are separated, and the transparent, nearly colourless liquid obtained by filtration is carefully evaporated. A transparent gummy mass results, which almost wholly dissolves in alcohol of 97 per cent. The alcoholic solution, by spontaneous evaporation, yields a syrupy, almost colourless product, which does not crystallize after standing several weeks. In this state it is evidently associated with some substance that prevents its crystallization. The syrupy liquid was agitated with several times its bulk of æther, but the former separated from the mixture unchanged. The difficulty of combining gaultherine with other bodies opposes a barrier to its examination.

As thus obtained, gaultherine has little if any odour, and a slightly bitter taste. When heated carefully on a plate of glass until all the moisture has evaporated, it remains as a transparent varnish-like layer, easily pulverizable. When held in a flame, it takes fire and burns tardily, with a large carbonaceous residue, and may be heated to 300° Fahr. without change; at 350° it froths and becomes darker coloured, and at 400° it becomes almost black and emits empyreumatic vapours. At the two first-mentioned temperatures the composition and properties of gaultherine do not appear to be affected, but at the latter they are almost entirely destroyed. Subjected to heat in a close tube, gaultherine is completely decomposed; a yellow oil condenses on the opposite end of the tube, which possesses the properties of oil of gaultheria, but is contaminated with pyrogenous matter; whilst a carbonaceous residue remains.

When gaultherine is mixed with concentrated sulphuric acid, it is dissolved, the acid acquires an intensely red colour, and the odour of the oil of *Betula lenta* is developed.

If gaultherine be distilled with diluted sulphuric acid, it is decomposed, and the distilled liquid is strongly impregnated with the oil, globules of which float upon its surface.

Distillation with dilute hydrochloric acid also generates the volatile oil.

When gaultherine is dissolved in dilute nitric acid (spec. grav. 1·04) and the mixture distilled, the liquid in the recipient contains no volatile oil; but floating on its surface and attached to the sides of the receiver are numerous acicular crystals of a pale yellow colour. This substance forms a yellow solution with alcohol, which by evaporation leaves it in minute crystals of a yellow colour. This substance is probably formed by the reaction in the receiver between the nitric acid vapour and that of the volatile oil (which is doubtless generated). It has an acid reaction, and appears analogous to the compound formed from the oil by nitric acid. When gaultherine is mixed with fuming nitric acid and gently heated, a rapid reaction takes place, nitrous acid vapours are evolved, and a yellow solution

results, which by mixture with water and standing deposits a crop of yellowish-white prismatic crystals.

The fixed alkalies and alkaline earths have a remarkable action on gaultherine, wholly destroying its power of generating volatile oil, and converting it into an acid, which remains combined with the base. When gaultherine is boiled with a solution of ammonia until the odour of the latter ceases to be perceptible, the gaultherine appears to be but slightly acted on, as it reacts with the residue of the bark, producing the volatile oil.

If gaultherine be boiled for some time with hydrated protoxide of lead in water, and the solution filtered, it is found to contain lead, and reacts alkaline. By adding sulphuric acid, carefully avoiding an excess, the liquid filtered from the sulphate of lead is acid, and does not contain sulphuric acid. But a small part of the gaultherine is decomposed.

The process of Piria for combining salicine with oxide of lead was tried with gaultherine, by rendering a solution of the latter alkaline with ammonia and adding subacetate of lead. The gaultherine was thrown down in combination with the oxide of lead; but it appears to be either converted into gaultheric acid, or otherwise decomposed, as neither the liquid filtered from the precipitate, or that obtained by decomposing the precipitate with dilute sulphuric acid, would yield the volatile oil when mixed with the residue of the bark.

Gaultheric Acid.—This acid is obtained by dissolving gaultherine in barytic water, boiling the solution for a short time, and afterwards passing a current of carbonic acid through the liquid until all the free baryta is removed, and filtering. A neutral solution of gaultherate of baryta is then obtained, from which the gaultheric acid may be isolated by cautiously adding dilute sulphuric acid as long as a precipitate is produced. The filtered liquid acts strongly acid on litmus, and does not precipitate baryta water. By evaporation it attains a thick syrupy consistence, and dries into a gum-like mass. In this form it is impure. By boiling it with carbonate of lead until saturated, filtering the solution, and then precipitating the lead with hydrosulphuric acid, a solution is obtained containing the acid in a much purer state, which by evaporation yields it in a nearly colourless mass, with some evidence of crystallization.

Gaultheric acid is soluble in water and alcohol, but is only slightly taken up by æther. It saturates acids, forming neutral salts, which do not crystallize.

By distilling it with dilute sulphuric acid, oil of gaultheria is obtained, and nitric acid appears to act on it like gaultherine.

The substance existing in the residue of the bark, after exhaustion by alcohol, and which reacts with gaultherine to produce the volatile oil, has not been isolated. It is insoluble in water, as by long maceration in that fluid it is not removed or changed. The temperature of ebullition entirely destroys its power of acting on gaultheria, which proves its analogy to synaptase. Maceration in solution of

potash, spec. grav. 1·05, also destroys its power. The impossibility of finding a menstruum capable of dissolving this principle has prevented a further examination of its properties.

In the foregoing observations some interesting facts have been elicited. The existence of a chemical compound of so extraordinary a nature as the salicylate of methylene in a diminutive individual of the heath tribe, was indeed striking; now we have the same complex substance pervading the bark, leaves, &c. of one of the largest of our forest trees. Additional interest attaches to the latter on account of a principle of a still more complex nature that exists in it, and which contains the elements of the salicylate of methylene; thus adding another to that class of neutral substances of which amygdaline is the type.

It will be interesting to know the ultimate composition of this principle, and the relation it bears to gaultheric acid and to salicylate of methylene. Before that can be accomplished, the necessity of obtaining it in a pure state is imperative. The more important of the observations contained in this paper were made during the last spring and summer; but till recently the author has not had sufficient leisure to arrange them for publication. It is hoped that the attention of chemists will be attracted to these principles, and their character more fully developed.

The results of my experiments tend to prove—

1st. The identity of the volatile oil of *Betula lenta* with the oil of *Gaultheria procumbens* (salicylate of methylene).

2nd. The existence of a peculiar principle in the bark of the *Betula lenta*, which bears the same kind of relation to the oil of gaultheria or *Betula lenta* that amygdaline bears to the oil of bitter almond; and to which I have given the name of *gaultherine*, as it gives rise to the oil of gaultheria by its decomposition.

The term *betuline* (perhaps more appropriate) has been already applied to another substance.

3rd. That there exists in the same bark, associated with gaultherine, a substance possessing the property of reacting with the latter so as to produce the volatile oil, and which is analogous in its mode of operation to synaptase, or emulsine.—*American Journal of Pharmacy* for Jan. 1844.

ANALYTICAL CHEMISTRY.

Employment of the Hydrate of the Protoxide of Iron in Eudiometry. By M. Dupasquier.

It is well known that the most easily executed of the various eudiometrical methods, *i. e.* the employment of phosphorus, is not accurate. The author strongly recommends the hydrate of the protoxide of iron, separated by caustic potash from pure protosulphate of iron, during the experiment itself. The following would be the plan for executing an analysis of the air with this substance:—The

requisite apparatus consists of a tube 15 millimetres broad and 30 centimetres long, which is closed at one end. A portion of the tube, comprising 50 cubic centimetres (therefore 27 centimetres long), is divided from the closed end into 100 equal parts; there remains therefore a piece at the other end 3 centimetres long; a hollow glass cap, 4 centimetres long, called the *obturateur*, and which is properly ground, is placed over this end. The tube is now filled with water, turned upside-down, and so much water allowed to flow out that the whole space between 0 and 100 is filled with air. If an abnormal quantity of carbonic acid is suspected in the air, a piece of caustic potash is placed in the hollow space of the glass cap, and the tube closed; it is then well shaken, opened under water, and the volume of carbonic acid absorbed noted. 2 grs. of caustic potash and 5 grs. of pure protosulphate of iron are now conveyed into the obturator, which is then dipped into water, the adhesive bubbles of air allowed to escape, and the apparatus closed. It is now shaken for half an hour in a horizontal position, again opened, and the volume of gas absorbed determined. The caustic potash employed must be pure and white, and not too strongly ignited, otherwise it contains peroxide of potassium, which disengages oxygen under water. The experiment is most accurate when the water is at the same temperature as the surrounding atmosphere. For very accurate researches an instrument may be employed, the total length of which is from 53 to 55 centimetres, the inner breadth 16 millimetres, the capacity of the graduated portion 100 cubic centimetres, the length of the obturator 5 centimetres, the depth of its cavity 3·5 centimetres. The degrees of this long tube may be also divided into fifths or tenths.

Recently-precipitated protoxide of iron has been said by some to possess the property of decomposing water; but this is an error; in water perfectly free from atmospheric air, and which has long boiled, the precipitate is only very slowly coloured.

The method of M. Dupasquier is, at all events, very simple and easily executed, and very advantageous for the examination of mixtures of gases containing oxygen and carbonic acid. The author assures us that the accuracy of the results is perfectly satisfactory. —*Ann. de Chim. et de Phys.* for Oct. 1843.

On Testing for Arsenic.

Otto (Ann. der Chem. und Pharm., xlii. 349) has made a very important remark with regard to the employment of caustic potash in the extraction of arsenious acid from organic matters, which had escaped the notice of those who had hitherto made use of this reagent. All substances which contain albumen and fibrine give with a solution of caustic potash a solution of proteine and potash, and sulphuret of potassium, which when arsenious acid is present in the mixture is converted into arsenio-sulphuret of potassium. If the filtered liquid be then supersaturated with hydrochloric acid, sulphuret of arsenic and proteine are precipitated; and if the quantity

be small, the whole of it may be lost, and if it be greater, still sufficient of it to form $As^2 S^3$ with the sulphur present is always lost. Otto mixed 1 gr. of arsenious acid with an egg and some boiled potatoes, and treated the solution with caustic potash, according to the usual directions. The fluid, precipitated with hydrochloric acid in excess, was *free from arsenic.*

This observation, the correctness of which is evident, must banish the employment of hydrate of potash in testing for arsenic, when organic substances containing sulphur are present.—Berzelius's *Jahresbericht,* xxiii.

Specific Gravity Balance.

We have received a communication from Sir James Murray, in which he claims being the first inventor and publisher of the instrument described in our last Number, p. 125, by Mr. F. Ham, for ascertaining the specific gravity of fluids. The instrument, we are informed, was exhibited and a description read before a large meeting of the College in Dublin, on the 25th of November last, a report of which was published in the Dublin Medical Press of Dec. 5th, 1843, and an abstract appeared in a free newspaper called the General Advertiser. We hasten to do justice to the claims of the honourable inventor, but at the same time we must express our regret that the instrument was not described in some other of the numerous channels of information more likely to meet the eye of the scientific chemist, as it can scarcely be expected that he should look into newspapers and strictly medical journals for information connected with his pursuits. Several of our chemical friends, to whom we showed Mr. Ham's communication previous to its insertion, were as ignorant as ourselves of its having been previously described.

PHARMACOLOGY.

Account of the Trees producing Myrrh and Frankincense. By Major W. C. Harris.

Major Harris describes the Myrrh-tree (*Balsamodendron Myrrha*) as growing abundantly on the Abyssinian coast of the Red Sea to the Straits of Bab el Mandeb, over all the barren hill-sides of the low zone inhabited by the Danakil or Adaiel tribes. It is called *Kurbeta,* and there exist two varieties; one producing the better description of the gum being a dwarf shrub, with deeply serrated crisp leaves of a dull green; while the other, which yields a substance more like balm than myrrh, attains a height of ten feet, and has bright, shining, slightly dentated leaves. The myrrh, called *Hofali,* flows freely from any wound, in the form of a milky juice, possessing a perceptible acidity, which either evaporates or becomes chemically

changed during the formation of the gum. The seasons for collecting it are in January, when the buds appear after the first rain; and in March, when the seeds are ripe. Every passer-by transfers such portions of it as he may find to the hollow boss of his shield, and exchanges it for a handful of tobacco with the next slave-dealer whom he meets on the caravan-route. The merchants also of the sea-coast, before returning from Abyssinia, send into the forests that gird the western bank of the river Hawash, and bring away considerable quantities of the *Hofali*, which is sold at a high price. The natives administer it to their horses in cases of fatigue and exhaustion.

The shrub which produces the balm of Mecca, *Balsamodendron Opobalsamum*, is found on the opposite Arabian coast at Cape Aden, where it is called *Beshán*, either the original of or a derivative from the word *Balsam*. It is the *Balessan* of Bruce, who did not meet with the true myrrh-tree. The balm flows copiously from any incision, and the æthereal oil speedily evaporating, a tasteless gum remains.

The Frankincense, Major Harris states, is found chiefly along the Somauli coast, in the neighbourhood of Cape Guardafui. At Bunder Maryah, twenty miles to the S.W. of Ras Feeluk, the mountains are three miles from the shore and attain a height of five thousand feet. Ascending a thousand feet a plain presents itself, bounded on every side by precipitous mountains, studded with the Frankincense and Gum-Acacia trees, although looking bare from the total absence of under-wood. The frankincense-trees invariably grow from the bare and smooth sides of the white marble rocks, or from isolated blocks of the same scattered over the plain, without any soil whatever. From the base of the trunk, and about treble its diameter, a round thick substance is thrown out, of a nature between bark and wood, adhering most firmly to the stone, and resembling at a distance a mixture of mortar and lime. The stem rises from the centre of this mass, and having first taken a bend outwards of several inches, rises straight to a height of forty feet. It throws out from the top short branches covered with a very bright green foliage, the leaves being narrow and rounded at the end, five or six inches in length by one broad, and crimped like the frill of a shirt, or rather like the sea-weed called by children on the English coast "the old gentleman's ruffles." The usual girth of the stem is from a foot to eighteen inches. The bark is perfectly smooth and consists of four distinct layers, the outermost of which is very thin; the two next of a singularly fine texture, resembling oiled letter-paper, perfectly transparent, of a beautiful amber-colour, and used by the Somaulis to write upon; and the innermost about an inch thick, of a dull reddish hue, tough and not unlike leather, but yielding a strong aromatic perfume. The wood is white and soft. On making a deep incision into the inner rind, the gum exudes profusely, of the colour and consistence of milk, but hardening into a mass by exposure to the air. The young trees produce the best and most valuable gum, the older merely yielding a clear glutinous fluid resembling Copàl varnish and exhaling a strong resinous odour. During the S.W. monsoon the pastoral tribes

in the neighbourhood of Ras Feeluk collect large quantities of frankincense, which they barter with the Indian Banyans, of whom a few reside at the villages along the Abyssinian coast. Boats from Maculla and from other parts of the Arabian coast also come across during the fine season and carry away the gums that have been accumulated, in exchange for a coarse kind of cotton cloth which is worn by the shepherds.—*Proceedings of the Linnæan Society.*

CHEMICAL PREPARATIONS.

Preparation of Protiodide of Iron. By M. Mialhe.

The author remarks that it is generally supposed that the above-named salt cannot be prepared in contact with the air and obtained solid in a state of purity, and he admits that in fact it generally consists of a mixture of variable quantities of protiodide, periodide and sesquioxide of iron and free iodine.

M. Mialhe states that the solid protiodide is easily prepared, even in contact with the air, by the following process:—prepare, in the usual manner, a solution of protiodide of iron, and evaporate it in a porcelain capsule, containing iron turnings or wire, quite free from oxide; the evaporation must be carefully conducted, and continued until a small quantity of the salt being taken up by a glass rod and deposited on a cool substance, it instantly solidifies. When this state of concentration is effected, the protiodide of iron is to be carefully poured off from the iron in the capsule, on a plate of glass or porcelain, and immediately afterwards introduced into small well-stopped dry bottles.

The properties of the protiodide of iron thus prepared are, that it is in the form of brittle scales of different degrees of thickness, which when broken exhibit evident traces of crystallization; it is extremely deliquescent; its solution is greenish; it is precipitated white by ammonia, and bluish-white by ferrocyanide of potassium; when triturated with starch no blue colour is produced.—*Journ. de Pharm. et de Chim.*, Janvier 1844.

Escharotic Solution of M. Freiberg.

℞ Camphor ..... 2 grammes.
Bichloride of mercury ..... 4 ...
Rectified alcohol ..... 30 ...

and dissolve.

This solution is employed in syphilitic vegetations, and especially against condylomata, in which it is very efficacious. The diseased portion is excised, and the solution applied with a brush.—*Journ. de Pharm.* for Feb.

A new Process for preparing Gallic Acid. By EDWARD N. KENT.

During a recent examination of black ink, which had been prepared by exposure to the atmosphere for three months, I found it contained a quantity of free gallic acid, protosulphate of iron and pertannate of iron.

Having previously experienced the inconvenience of waiting two months to prepare gallic acid by the old process, and as it is not an article of commerce, it occurred to me that if the acid in the ink could be easily isolated, it would form a valuable process for its preparation when wanted for immediate use, as ink can always be readily obtained containing the acid ready formed. I therefore agitated a pint of ink with an equal measure of sulphuric æther*, left it at rest for a few moments to separate, and then decanted the æther, and found it had taken up gallic acid to the exclusion of the other constituents, except a light yellow colour and odour of cloves, these having been put into the ink. I then distilled the æthereal solution nearly to dryness; the residue crystallized on cooling. I returned the distilled æther on the ink, and repeated the process the third time; and after crystallizing three times and drying, obtained 28 grs. of colourless gallic acid.

I then distilled off from the ink a little remaining æther, and the ink was left as good for *ordinary* purposes as before; and the only expense in the preparation of the acid was the loss by evaporation of about 1 oz. of the æther.

Most of the inks which I have tried gave the same result when treated with æther. Some however which have been prepared by boiling the nutgalls, and exposure for a few days only, yielded principally tannic acid. It is therefore advisable to test the ink with gelatine before attempting to prepare gallic acid by this process.—Silliman's *Journal* for Jan. 1844.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Jan. 1, 1844. (The President in the Chair.) The following communications were read:—

"An Account of a Class of double Sulphates containing Soda and a Magnesian Oxide," by Alexander R. Arrott, Esq.

In this paper the author, after alluding to the fact that double salts of soda and the magnesian metals are not formed by spontaneous evaporation of a mixed solution of their constituent salts, describes

* Mr. Silliman, Jun. states that he has repeated Mr. Kent's experiment successfully. He observes that care must be had that the æther is quite free from alcohol, which commercial æther never is. As gallic acid is more soluble in alcohol than in æther, the process is only partially successful when alcohol is present.

a method by which they may be readily produced, namely, by evaporating these at temperatures exceeding 100°. In this way salts of soda and magnesia, zinc, iron, copper and manganese were formed. The first three contained 4 atoms of water, and the copper and manganese 2 atoms.

These salts are persistent in air, are not altered by a temperature of 212°, but are decomposed when dissolved in cold water.

The copper salt is decomposed when boiled, and an insoluble subsalt precipitates.

The cause why no double salt is formed at low temperatures is supposed to be the assuming of water by the sulphate of soda, and the inability of the hydrated sulphate to enter into such combinations; this is avoided by the use of a high temperature, sulphate of soda then becoming anhydrous.

"Experiments on the Heat disengaged in Combinations.—Part II. Neutralization of various Acids by Hydrate of Potash." By T. Graham, Esq.

The same arrangements were used in these experiments as in the first series, except that the quantity of water was increased from 1000 grs. to 1544 grs. (100 French grms.) and a thermometer of larger divisions employed, graduated according to Fahrenheit's scale.

The neutralization of an equivalent of nitric acid by potash was attended by the disengagement of 10·50 degrees Fahr. of heat; of hydrochloric acid by the same base 10·26 degrees; the experiments being made about the temperature of 63° Fahr. But the heat disengaged diminishes at lower temperatures; thus at 40° Fahr. the heat disengaged on saturating nitric acid was 10·38 degrees, or it is diminished 1·2 per cent. by lowering the temperature of the experiment 23°.

The large proportion which the cold produced on dissolving in water crystallized nitrate of potash and chloride of potassium, the combinations formed in these experiments, to the heat observed, was pointed out; the cold, on dissolving at 63° an equivalent of nitrate of potash in the usual quantity of water, being 5·72 degrees. This fall of temperature however is not constant, but increases with the lowness of the temperature of the water in which the crystallized salt is dissolved, being 5·72 degrees at 63° Fahr., 5·94 degrees at 43°. Here a difference of about 20° in the temperature of the water makes a difference of one-twenty-seventh part in the cold produced on dissolving the salt.

On the other hand, the cold, on dissolving several equivalents of nitrate of potash successively, at a constant temperature, in the same quantity of water, diminishes greatly with the number of equivalents of salt dissolved. Thus while the first equivalent occasions a fall of only 5·72 degrees at 63°, the sixth equivalent occasions a fall of only 3·82 degrees at the same temperature. The full fall of temperature however occurs on diluting the last solution with water. This decreasing rate was shown to continue in salts of greater solu-

bility, such as nitrate of ammonia and nitrate of soda, of which a large number of equivalents may be successively dissolved in the same water; the cold from the solution of an equivalent of either of these salts being reduced to about one-third as the solution approached saturation. In these and other anhydrous salts, which produce great cold on dissolving, only a small absorption of heat is therefore actually occasioned by the liquefaction of the solid salt, the greater part being due to the subsequent combination of the liquefied salt with more water, that is, to dilution of the solution.

When 2 equivalents of sulphuric acid are neutralized by potash, 22·76 degrees of heat are disengaged, of which 10·38 degrees are disengaged by the first equivalent of alkali in the formation of bisulphate of potash, and 12·38 degrees by the second, which neutralizes the excess of acid in the bisulphate. The solution of sulphate of potash in acidulated water produces more cold than in pure water. The same is true of the magnesian sulphates, such as sulphate of magnesia, zinc, copper and iron. Strong solutions also of these salts, as well as of sulphate of water, produce heat, and not cold, when diluted with water.

PATENT.

Patent granted to James Clement, Liverpool, *for improvements in Composition for ornamenting Glass and Picture-frames, and Articles for Decorations; also for the Manufacture of Toys.*

The invention for which this patent has been obtained consists in producing a composition or compositions, to be applied to ornamenting glass and picture-frames, and articles for interior and other decorations, and for making toys, &c., by combining the paste or pulp of potatoes with any other suitable materials in a pulverized state.

The potatoes are boiled, steamed or roasted, as if intended for the table, and are then bruised and mixed with some finely pulverized substance, such as sawdust, turf, the waste bark from a tan-yard, or any other fine powder that can be obtained at a small cost. This mixture is worked into a fine paste by rolling and beating, and is then ready to be moulded into the required forms.—Sealed March 4, 1842.

THE CHEMICAL GAZETTE.

No. XXXV.—April 1, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a New Sulphate of the Peroxide and Protoxide of Iron. *By* M. Abich.

This salt is obtained in the following manner:—16 parts of pure crystallized protosulphate of iron are dissolved in water to form a moderately concentrated solution, which is mixed with an equal weight of concentrated sulphuric acid; it is then heated to boiling, 1 part of strong nitric acid and a concentrated solution of from 5 to 6 parts of alum added to it. When the solution is evaporated over a water-bath at a temperature not exceeding 158°, a dark green crystalline powder separates; the mother ley is poured off and the powder redissolved with the assistance of a gentle heat, in water strongly acidulated with sulphuric acid. On slowly evaporating this solution black crystals are formed at the bottom and on the surface of the liquid, where they form a crust which subsequently subsides. These crystals belong to the regular system, and form a combination of the octahedron with the hexahedron. This salt is washed with strong alcohol to remove the water and acid, and dried quickly. The colour is actually a dark green, but it approaches to black. The surfaces of the crystals have a diamond lustre. It may be preserved in dry air, for instance, in a well-stoppered bottle; but when exposed to the ordinary air it absorbs moisture, and acquires a dull appearance from the surface becoming covered with minute crystals of $Fe^2 O^3, SO^3$. The salt is composed of $3\,(FeO, SO^3) + 2Fe^2 O^3, 3SO^3$ and the crystals contain 2 atoms of salt combined with 9 atoms of water, which amount to 15·94 per cent. On analysis 14·16 per cent. was obtained, so that if we suppose 1 per cent. of the water to arise from the mother-ley inclosed in the crystals, each atom of salt would contain 4 atoms of water. M. Abich observes that he was not able to obtain this salt without a small portion of the peroxide of iron being replaced by alumina; according to his analysis, 2·2 per cent alumina to 17·65 per cent. peroxide of iron: it is on this account that alum is added. When the solution of the salt in acid water is evaporated too quickly the formation of crystals is prevented, and only micaceous scales are obtained, which contain a less amount of water. This can be prevented by adding, on redissolving the pre-

cipitated salt in acid water, a quantity of crystallized sulphate of copper equal to $\frac{1}{16}$th the weight of the protosulphate of iron employed, none of which however is taken up by the crystals.—Berzelius's *Jahresbericht* xxiii. p. 214.

On the Quantity of Carbonic Acid expired by Man, from the Experiments of Andral *and* Gavarret, Scharling, Brunner *and* Valentin, *as well as the Remarks of the latter on the Theory of Respiration.*

The question of the quantity of carbonic acid expired by a person in twenty-four hours, which has again become of extraordinary interest in consequence of the late advances in physiological chemistry, has been answered almost simultaneously from several quarters. The calculations of Lavoisier and Seguin, based on the supposition that the respiratory process is perfectly uniform, have hitherto been received, because those of Davy, Allen and Pepys appeared too high. According to their observations a man inspires 15,661 grs. of oxygen, and expires 8584 grs. of carbonic acid (= 2820 grs. of carbon) in twenty-four hours. Prout has however shown that the former statement is erroneous, that, for instance, the quantity of carbonic acid expired during the night is less.

Liebig endeavoured indirectly to estimate the quantity by comparing the amount of carbon contained in the food consumed during the twenty-four hours with the carbon of the excrements voided in the same time, and estimating the difference as the quantity separated by the respiratory process. He thus found that an adult, taking moderate exercise, expired daily on an average 13·9 oz. of carbon (more than double the quantity found by Lavoisier). All this rendered a repetition of the examinations requisite.

Experiments made for this purpose have, as is well known, to overcome great difficulties, for the apparatus which collects the products completely at the same time generally renders the breathing irregular. We will now see how the different experimenters endeavoured to solve this problem.

Andral and Gavarret adopted the method proposed by Dumas and Boussingault. They fitted a mask air-tight to the face, and tubes communicating with this were so arranged that the air could be inspired through two of them (a valve preventing the air from escaping during expiration); the third, which transmitted the expired air, was provided with a stopcock, and connected with three exhausted balloons; the cock being turned during expiration, the air was allowed to escape through the tube, which was closed by the cock during inspiration.

The necessary calculations were made for temperature and barometric pressure, and each experiment was continued from eight to thirteen minutes. The expansive coefficient of the air was considered as = ·00366. In each experiment about 130 litres of dried gas were collected. The products were passed over a mixture of sulphuric acid and pumice-stone, and solution of potash in a

Liebig's apparatus. The only error in these experiments was the amount of carbonic acid being estimated rather too highly on account of some undecomposed air remaining in the apparatus; but this was found to be so inconsiderable as not to interfere with the general results.

Scharling proceeded in an entirely different manner. He used a box, in which the person experimented upon was inclosed air-tight. Tubes passed into the top and bottom of this box; and in the lowest tube, admitting the air into the box, solution of potash was contained, to deprive the air of any carbonic acid. The expired air was passed through sulphuric acid, solution of potash, and lime water, to deprive it of all moisture and carbonic acid. The quantity of carbonic acid in the box at the commencement and termination of the experiment was estimated by glass tubes filled with mercury, &c. The persons experimented upon were amused by working, reading, &c., and every precaution was taken to keep the respiration perfectly free and normal. The experiments never lasted more than an hour.

Brunner and Valentin, who attended less to the absolute quantity of carbonic acid, but rather to its relation to the inspired oxygen, did not in their experiments insure so perfect a freedom of the respiratory process, as they prevented any loss of the collected gases. They made use of two different kinds of apparatus. In the first method the expired air was passed through asbestus moistened with sulphuric acid, thence into a three-necked bottle. The air in the latter was expelled by displacement, being forced out by the expired air. The expiration was continued for fifteen minutes, when it was concluded that no other than the products of expiration existed in the bottle. This was then passed through asbestus and acid, a phosphorus eudiometer, and a tube containing freshly-hydrated lime, and sulphuric acid and pumice-stone (the lime and acid were separated by pieces of porcelain and cotton), and finally a bottle containing lime-water. The air was forced out of the bottle by pouring mercury through a funnel fixed in its middle neck. In each experiment 618·457 cubic centimetres of expired air were analysed in the space of from twenty to thirty minutes. In calculating the results, the weight of 1 litre of oxygen at 32° Fahr. and ·76 barom. was considered as = 1·4323 grm.; of 1 litre of carbonic acid = 1·2675 grm.; and of 1 litre of nitrogen = 1·2675 grm.: the coefficient of expansion of the air, oxygen and nitrogen, was estimated as ·0103665, and of carbonic acid ·00369087. The amount of inspired air was separately ascertained from the volume of nitrogen, which remained as the difference of weight after the volume of oxygen and carbonic acid had been found.

In their second experiments, a bottle holding 15000 cubic centimetres was used, and filled with salt and water. Expiration was made into this bottle with the nostrils closed, inspiration being made through the open nostrils; the bottle became filled with the products of expiration in from fifteen to eighteen minutes. The breathing-tube was then removed, and the expired products passed through

tubes containing sulphuric acid and pumice-stone, lime-water, and lastly, a phosphorus eudiometer. An aspirator filled with oil concluded the apparatus. Upon allowing the oil to escape, the air was drawn through the system of tubes, and became deprived of its oxygen and carbonic acid, the nitrogen alone remaining. The results are calculated as above. Salt water is used because it absorbs very little carbonic acid. In each analysis 529·42 cubic centimetres of carbonic acid were forced through the apparatus. If the tube containing the lime, on using this apparatus, is weighed at the commencement, the absolute quantity of carbonic acid expired can then be found, provided the time has been noticed in which the volume of carbonic acid was breathed.

RESULTS:—A. *Absolute Quantity of expired Carbonic Acid.*

Andral and Gavarret expressed their results per hour. They are contained in the following table:—

Male Sex.

Age.	Muscular development.	Carbon consumed per hour. grms.
8	Moderate	5·0
10	Very great	6·8
12	Moderate	7·4
12	Great	8·3
14	Moderate	8·2
16½	Good	10·2
18	Good	11·1
20	Good	10·8
24	Moderate (mean of 2)	11·5
26	Extraordinarily great	14·1
		14·1
26	Moderate	11·0
28	Good	12·4
32	Good	11·5
33	Moderate (mean of 6)	10·7
37	Moderate	10·7
40	Very great	12·1
45	Very slight (mean of 4)	8·6
48	Good	10·5
50	Good	10·7
54	Very great	10·6
59	Moderate	10·0
60	Extraordinarily great	13·6
63	Extraordinarily great	12·4
64	Slight	8·7
68	Moderate	9·6
76	Slight	6·0
92	Extraordinarily great	8·8
102	Extremely diminished	5·9

Female Sex.

Periods of life.	Age.	Muscular development.	Carbon consumed per hour.
Prior to the appearance of the catamenia.	10	Good	6·0
	11	Good	6·2
	13	Great	6·3
	15½	Very great	7·1
During menstrual life.	15½	Moderate	6·3
	19	Very great	7·0
	22	Good	6·7
	26	Slight	6·0
	26	Moderate	6·3
	32	Moderate	6·2
	45	Moderate	6·2
After cessation of catamenia.	38	Moderate	7·8
	42	Good	8·3
	44	Very great	9·9
	49	Moderate	7·4
	52	Moderate	7·5
	56	Moderate	7·1
	63	Moderate	6·9
	66	Moderate	6·8
	76	Very great	6·6
	82	Moderate	6·0
3 months pregnant.	42	Good	7·8
5 m. do.	32	Good	8·1
7½ m. do.	18	Slight	7·3
8½ m. do.	22	Good	8·4

It is thus seen that in general the amount of carbonic acid expired by both sexes increases with age up to a certain point, the 40–45th year, and then diminishes; that the quantity of carbonic acid expired especially increases with the development of the muscular system; that women expire less carbonic acid than men; that the formation of carbonic acid attains its maximum at the commencement of menstruation, and then experiences no further increase, except in the pregnant state, until the cessation of menstruation, when an increase again takes place. On an average an adult male, of moderate constitution, consumes 10·5–11 grms. of carbon per hour; an adult female in the unimpregnated state 6·5–7; during pregnancy 8; and after the cessation of the catamenia 7·5–8·5. Dumas also found 10 grms. per hour as the average quantity of carbon consumed by an adult male.

Scharling's experiments were made on the following individuals:—1st, a male æt. thirty-five, weighing 131 lbs.; 2nd, a male æt. sixteen, weighing 115½ lbs.; 3rd, a soldier æt. twenty-eight, weighing 164 lbs.; 4th, a girl æt. nineteen, weighing 111½ lbs.; 5th, a boy æt. nine and three-quarters, weighing 44 lbs.; and 6th, a girl æt. ten, weighing 46 lbs. The carbon consumed per hour amounted to—

No. of the person.	Amount of carbon. grs.	Remarks.
1.	145	Fasting
In June when very hot.	190	After breakfast and a walk
	130	Hungry
	165	2 hours after dinner
	160	After tea
	100	Whilst asleep
2.	114	Sleepy
In June when very hot.	144·2	Fasting
	139·8	Fasting and hungry
	177	½ an hour after breakfast
	167·7	2½ hours after breakfast
	180·8	2 hours after dinner
3.	137·8	Asleep
In October.	111·9	Fasting
	159·4	Fasting, after breakfast and work
	188·9	After dinner
	194·7	3 hours after dinner
	178·3	After work
	122·3	Whilst asleep
4.	98·9	Whilst eating
In October.	91·3	Fasting
	92·6	After supper
	133·8	1 hour after breakfast
	117·0	1 hour after dinner
	108·9	Whilst eating
5.	76·2	Fasting
In Autumn.	94·8	Whilst at breakfast
	113·8	After breakfast
	119·3	1 hour after dinner
	84·5	2 hours after supper
	74·8	Whilst sleepy
6.	65·5	Whilst asleep
In Autumn.	95·3	After breakfast
	103·0	After dinner
	99·0	Shortly after tea
	75·1	Whilst asleep

Supposing that adults sleep seven, children nine hours per day, the amount of carbon consumed is on an average—

	In twenty-four hours. grms.	In one hour. grms.
1.	219·47	9·188
2.	224·37	9·389
3.	239·71	9·980
4.	165·88	6·812
5.	133·13	5·517
6.	125·42	5·226

It is thus evident that the quantity of carbonic acid expired is very variable, and that a number of circumstances are able to alter it. Hunger and repose diminish, satiety and labour increase it; it is greater during the day than the night (about 1·24 : 1).

In other respects the results agree accurately with those of Andral and Gavarret, if we recollect that they experimented only during the day, whilst the above numbers give the average of both day and night. The differences between the maximum and minimum observed by the same authors, are as 1·5 : 1 to 1·74 : 1, as a mean 1·616 : 1.

If the expired carbonic acid is estimated in relation to the weight of the body, it is found that children consume somewhat more carbon than adults. Sickness diminishes the amount of carbonic acid. The consumption of carbonic acid is modified principally by the fitness of the respiratory organs in each case to carry on the process, and the state of the circulation.

The influence of muscular activity on the amount of carbon consumed, has been clearly shown by some experiments made by Dr Hofmann during a pedestrian tour. His diet was simple and scanty, he took no drink, walked during the whole day, weighed all his food and every excretion which was possible (even the nasal mucus), as well as himself; he then found that the weight lost by the body was never equalled by the excess of the excrements over the food, and that there was a constant loss of matter by the skin and lungs which amounted to more than 1 lb. We must pass over the details of his experiments. Brunner and Valentin found that the weight of carbon they consumed per hour was = 8·7–11·0 grms., on an average 10·4. The volume of expired carbonic acid per hour on an average was equal to 21·8 litres, and the volume of the air altogether which was expired per hour was = 540 litres on an average. These results agree well with those of the earlier observers. When the corrections for moisture are made, the quantity of carbon expired per hour is equal on an average to 11·2 grms., and of carbonic acid 28·5 litres.

B. *Relations of the Constituents of the expired Air altogether to the Theory of Respiration.*

On this point Brunner and Valentin only have experimented. They found—

Individual.	Number of experiments.	Volume per cent. CO^2.	O.	N.	Volume per cent. in relation to the atmosphere. Disappeared O.	Difference of N.	Weight per cent. CO^2.	O.	N.	Volume per cent. in relation to the atmosphere. Disappeared O.	Differ. of N.
Brunner.	Mean of 12 experiments, 1st series	4·356	16·007	79·547	4·720	+ 0·362	6·522	17·428	76·050	5·582	−0·940
	Mean of 4 experiments, 2nd ...	3·825	16·306	79·869	4·508	+ 0·683	5·749	17·735	76·516	5·275	−0·474
Thomas.	Mean of 4 experiments, 1st ...	4·673	15·895	79·432	4·920	+ 0·329	6·975	17·165	75·860	5·845	−1·130
Valentin.	Mean of 2 experiments, 1st ...	4·316	16·143	79·541	4·671	+ 0·356	6·458	17·481	76·061	5·529	−0·929
	Mean of 12 experiments, 2nd ...	4·641	15·783	79·576	5·032	+ 0·391	6·945	17·089	75·965	5·920	−1·025
	Total average	4·380	16·033	79·587	4·783	+ 0·402	6·546	17·373	76·081	5·637	−0·909

It is thus next evident, that the variations observed in the amount of nitrogen are entirely within the errors of observation, and the nitrogen may be considered as inactive.

Again, the expired air contains a volume of carbonic acid, which is but little less than the volume of oxygen which has disappeared (therefore the weight per cent. of the carbonic acid is necessarily somewhat greater than that of the absorbed oxygen, and thus also the difference of nitrogen appears positive as regards volume, but negative as regards weight); so that all the oxygen absorbed reappears as carbonic acid, except a small quantity consumed in the body for other purposes. Now, according to Graham's law of the diffusion of gases, when they are separated by an animal membrane and are under equal pressure, they become mixed inversely as the square roots of their densities; consequently 1·17585 volume of oxygen is absorbed for one volume of expired carbonic acid. Comparison of the figures shows us that the mixture of the two gases in respiration takes place entirely according to the law of diffusion of gases; for a method of experimenting, as accurate as possible, gave results in which the figures obtained for the carbonic acid and absorbed oxygen almost exactly agreed with those reckoned according to the law of the diffusion of gases:—

Volume per cent. of the expired air. CO^2.	O.	N.	Oxygen absorbed.	Carbonic acid calculated.	Difference.
3·850	16·270	79·185	4·690	3·994	+ 0·144 per cent.
3·593	16·034	79·185	4·931	4·199	+ 0·606 ...
3·949	16·090	79·185	4·887	4·162	+ 0·213 ...
3·777	16·090	79·185	4·914	4·192	+ 0·415 ...
3·759	16·095	79·185	4·922	4·192	+ 0·433 ...
4·483	15·328	79·185	5·698	4·853	+ 0·370 ...
4·752	14·733	79·185	6·362	5·418	+ 0·660 ...
4·588	14·852	79·185	6·253	5·325	+ 0·737 ...

In respiration, which is consequently a purely mechanical process, the inspired air is first warmed to 99°·5 Fahr., and saturated with moisture at this temperature, which is rapidly accomplished on account of its extensive distribution. It then experiences a simple diffusion; the nitrogen remains entirely unaffected; 1·1742 volume of oxygen is absorbed, and replaced by 1 volume of carbonic acid which is expired, or for each volume of oxygen absorbed 0·8516 volume of carbonic acid appears. In consequence of the accuracy with which the law of diffusion is here observed, the most minute portion only of other gases is absorbed or expired.

That hydrogen, carburetted hydrogen and carbonic oxide gases are not contained in the expired air, the authors have shown by some direct experiments; but small quantities of organic matters during respiration are evolved, as is shown by sulphuric acid, through which the expired air passes, being always coloured red. It need hardly be mentioned, that the authors, in calculating the results, adopted every precaution to insure accuracy, and made every necessary correction. For further details we must refer to the original treatises.—Andral and Gavarret, *Ann. de Chim. et de Phys.*, Trois. Sér. 8 Juin 1843, pp. 129–150; Scharling, *Ann. der Chem. und Pharm.*, xlv. pp. 214–242; Hofmann, *Ibid.* pp. 242–249; Brunner and Valentin, *Medicinische Vierteljahrsschrift*; *Archiv für Physiol. Heilk.* von Roser und Wunderlich. Zweiter Jahrgang, 1843. Heft iii. pp. 373–417.

Quicksilver from China.

Considerable interest was excited yesterday at the North and South American Coffee-house by the exhibition of a sample of quicksilver from China, a large quantity having been received by Messrs. Baring. It was brought to this country in large bamboo canes, the ends of which were stopped with resin, and packed in cases in an upright position. The wood of the bamboo did not appear at all injured, and none of the subtle mineral (which was declared of a very superior quality) had escaped.—*Morning Chronicle*, March 29, 1844.

Examination of some Lichens. By F. Rochleder and W. Heldt.

The authors recommend for the extraction of the substances contained in lichens, a mixture of ammonia and aqueous alcohol.

1. *Evernia prunastri.*—If this lichen is allowed to remain some minutes in contact with ammoniacal alcohol in a closed vessel, the liquid then passed through a linen strainer, a third part of water added, and the ammonia neutralized by acetic acid, gray flakes are precipitated, which are washed with water by decantation, dried at 212°, and crystallized several times from absolute alcohol. This substance is sometimes contaminated by small quantities of another body, which may however be separated by solution in æther, when it remains behind.

The substance soluble in æther, warm alcohol and in alkalies, and crystallizing in minute white needles, is lecanorine; for on dry distillation it afforded a product containing orcine, on boiling with barytic water it gave carbonate of barytes, by treatment with hydrochloric or sulphuric acid and alcohol a body was obtained which crystallized in shining laminæ; it moreover afforded on analysis 60·22 per cent. C and 4·79 H; the formula $C^{18} H^8 O^8$ requires 60·28 and 4·4. On precipitating the boiling alcoholic solution of lecanorine with sugar of lead, a plaster-like precipitate is obtained, which is sparingly soluble in alcohol, and contains 37·71 C and 2·73 H = $C^{18} H^4 O^8$, PbO.

Chloride of calcium produces in an ammoniacal solution of lecanorine a gelatinous precipitate soluble in alcohol and in water; acids throw down white flakes of lecanorine from its solutions. On boiling lecanorine for some time with nitric acid, it affords, with evolution of red vapours, a syrupy acid liquid, which contains much oxalic acid.

If dry muriatic acid gas be passed through a boiling saturated solution of lecanorine in absolute alcohol until no more is absorbed, the liquid warmed in the water-bath for some time, and then water added to it, a blackish-green resinous substance is precipitated, from which boiling water extracts, as observed by Mr. Schunck, pseudoerythrine, which separates on cooling in shining, iridescent, crystalline laminæ; these were found to consist of 61·65 C and 6·38 H ($C^{22} H^{13} O^9$). If we compare the formula of pseudoerythrine with that of lecanorine, the former will appear to be lecanorate of the oxide of ethyle ($C^{18} H^8 O^8 + C^4 H^5 O$), if we regard lecanorine as lecanoric acid; and, in fact, when pseudoerythrine is dissolved in barytic water, a few drops of caustic potash added to the solution, and the whole heated in a retort, a considerable precipitate of carbonate of barytes is formed, while alcohol passes over. The solution filtered from the carbonate of barytes becomes red by exposure to the air with ammonia, and therefore contains orcine. This decided proof of the pre-existence of the oxide of ethyle and lecanorine in pseudoerythrine likewise explains the disappearance of the latter, as observed by Dr. Kane, on boiling the aqueous solution for a length of time.

The fibre of the lichen was isolated, after having exhausted the plant with alcohol and æther, by extracting with cold alcoholic solution of potash, boiling with a dilute aqueous solution of caustic potash, washing thoroughly with water, then with dilute muriatic acid, and finally with boiling water. The substance, which had swelled considerably, was boiled with absolute alcohol, when it contracted very much; it was dried at 212° and pulverized. The grayish powder, which was void of smell and taste, contained 2·216 per cent. ash, 46·01 C, 6·63 H, and 47·36 O.

2. *Lichen rangiferinus*, E.—On treating this lichen in the same manner as the preceding, a crystalline substance separates on saturating the ammonia with acetic acid, which is obtained pure by recrystallization from boiling alcohol. This substance is procured

by extracting the lichen with æther. Knop first detected it in the *Usnea florida*, and has called it usnine or usnic acid. It forms minute, silvery, slightly yellowish acicular crystals, void of taste, and difficult of solution in alcohol and æther at the ordinary temperature; it is represented by the formula $C^{38}\,H^{17}\,O^{14}$; it differs therefore from lecanorine in this, that 2 equivalents of the latter must give off O^2 and receive $C^2\,H$, in order to form usnine. Notwithstanding this resemblance, however, usnine affords no orcine on dry distillation; on boiling it with a solution of potash the liquid gradually becomes red; acetic acid then separates yellowish resinous flakes; on longer boiling the solution becomes brown, and acids now precipitate brown flakes, which are soluble in alcohol and combine with oxide of lead. The boiling alcoholic solution of usnine gives a precipitate with basic acetate of lead, which contains 5 equivalents of oxide of lead and 2 of usnine. M. Knop has entered into a minute investigation of usnine, which will be published in our next Number.

The skeleton of the *L. rangiferinus* gave 1·602 per cent. ash, 46·28 C, 6·75 H.

3. *Usnea barbata*, Fr.—This lichen contains usnine (64·01 C, 4·83 H), and affords, on removing the envelopes surrounding the fibres and exhaustion with solvents, a skeleton mass, which contains scarcely any ash and was composed of 46·47 C and 6·67 H.

4. *Ramalina calicaris*, Fr. a, *fraxinea*; b, *fastigiata*.—Both varieties contain usnine. The skeleton was composed of 5·4 per cent. ash, 45·76 C, 6·78 H.

5. *Lichen parietinus*, L.—Herberger found in this lichen, besides fat, chlorophylle, &c., two crystallizable colouring substances, one yellow and the other red, which could be extracted with boiling alcohol. If the lichens be treated as above, with ammoniacal spirits of wine or an alcoholic solution of potash, and the filtered solution neutralized with acetic acid, yellow flakes are obtained, which are washed with water, redissolved in alcoholic solution of potash, precipitated by acetic acid, washed, dried at 212°, boiled with a little absolute alcohol, and then placed aside to cool.

On repeating this treatment, radiately grouped or interwoven yellow needles of a golden lustre are obtained in small quantity, to which the authors apply the name of *chrysophanic* acid. It consists, dried at 212°, of—

	Found.		Equiv.		Calculated.
Carbon	68·45	68·65	10	= 758·54	68·45
Hydrogen ..	4·56	4·59	4	= 49·92	4·50
Oxygen			3	= 300·00	27·05
				1108·46	

Chrysophanic acid dissolves in cold æther and alcohol with a yellow colour, in aqueous alkalies sparingly and with a red colour; it is abundantly soluble in boiling alcohol and æther, and in alcoholic solutions of potash and ammonia. The splendid red alkaline solutions are precipitated yellow by acids.

In closed vessels the acid is sublimed, partly undecomposed, in yellow needles. The solution in potash may be evaporated, without decomposition, to dryness; at a certain degree of concentration the potash salt separates in blue flakes with a violet tint, which dissolve in water and alcohol again with a red colour. The ammonia compound is decomposed on boiling, the acid being left behind unaltered. Dilute nitric acid does not even decompose chrysophanic acid on boiling, but concentrated nitric acid affords a red body, which dissolves in ammonia with a most beautiful violet-red colour. On boiling with a solution of caustic potash, a violet body, insoluble in water, is formed with evolution of ammonia. The combinations with barytes and oxide of lead are insoluble in water, but are decomposed by the carbonic acid of the atmosphere. An alcoholic solution of basic acetate of lead produces in boiling alcoholic solutions of chrysophanic acid at first only a faint whitish precipitate, which disappears on the addition of water and boiling; while at the same time carmine-red voluminous flakes are thrown down, which are insoluble in water, are decomposed by washing with alcohol, and when dry and pulverized form a vermilion powder. It is however not possible to dry it without partial decomposition, and it is on that account that the results of the analysis of this salt, dried at 212°, vary in the amount of oxide of lead from 56·73 to 59·32 per cent.

The yellow colour of the *Lichen parietinus* does not however disappear on the complete exhaustion of the chrysophanic acid, and results from a viscid colouring substance soluble in alcohol but not crystallizable. The skeleton contained 11·32 ash and 45·88 C, 6·55 H.

From this investigation we are made acquainted, in the first place, with the affinity between lecanorine, orcine and pseudoerythrine, so that we are compelled to admit that probably in all the lichens which afford the two latter substances lecanorine was originally contained; a second substance, widely distributed in several species of lichens, is usnine; and a third, the chrysophanic acid.

The skeleton substance of all the species of lichens examined has the same composition:—

	Mean.	Equiv.		Calculated.
Carbon	46·08	36	= 1730·70	46·15
Hydrogen	6·67	31	= 386·86	6·54
Oxygen	47·25	28	= 2800·00	47·31
			5917·56	

According to an experiment of Professor Liebig, the skeleton of *Cetraria Islandica* affords sugar on boiling with dilute sulphuric acid. If we subtract from $C^{36}\,H^{31}\,O^{28}$, $2C^{12}\,H^{11}\,O^{11}$, there remains $C^{12}\,H^{9}\,O^{6}$, *i. e.* 3 equiv. acetic acid less 3O. The employment of *Lichen rangiferinus*, and of other lichens poor in starch, as food, may probably depend on the capability of the skeleton being converted into sugar.—*Ann. der Chem. und Pharm.*, xlviii. p. 1–18.

ANALYTICAL CHEMISTRY.

On the Detection of Arsenic. By MM. Duflos and Hirsch.

A small work has appeared by Duflos and Hirsch*, on testing for arsenic in general, which in a space of fifty pages gives a clear and complete account of the various methods hitherto used or proposed for the detection of the presence of arsenic in medico-legal proceedings. They consider that Marsh's test is not the most certain, but give the preference to the precipitation with sulphuretted hydrogen, and the reduction of the arsenic from the sulphuret. Their mode of proceeding is succinctly as follows:—

The suspected mass, in which arsenious acid in its solid state shall not have been found (a stomach with its contents for instance), after having been cut in pieces, is placed in a tubulated retort with an equal weight of muriatic acid (which must have been previously ascertained to be free from arsenic by testing it with sulphuretted hydrogen), the retort connected with a receiver containing a little water, and the greater part of the liquor distilled off in a bath of chloride of calcium, until in fact the mass in the retort assumes the consistence of pap. After it has become cool, this is carefully mixed with twice its weight of strong alcohol (alcohol of about 90 per cent.), and set aside for some time; after which the solution is brought on a filter, and the residue well washed with alcohol.

The alcohol is now distilled off from this filtered solution, and the residue added to the acid liquor which passed over into the receiver during the first distillation, and which might possibly contain a little chloride of arsenic.

The liquid is now treated with sulphuretted hydrogen, and allowed to stand in a vessel, lightly covered, at a temperature of 120° to 140°, until all excess of sulphuretted hydrogen has evaporated. It is then filtered, and the sulphuret of arsenic received on the filter. Should it be too small a quantity to be removed from the filter, it must be dissolved in caustic ammonia, the solution evaporated to dryness in a porcelain capsule, and the residue treated with nitric acid of 1·34 to 1·40 spec. grav., and again evaporated to dryness; thereupon the mass is mixed with from 6 to 8 times its weight of well-carbonized cream of tartar (black flux), and the mixture made into a paste with a little water, and spread upon a strip of window-glass of about 1½ to 2 lines broad, and well dried.

This is now placed in a glass tube of 3 lines diameter, which is drawn out at one end into a finer tube, and hydrogen gas passed through it, which has been previously led through a tube containing cotton-wool, moistened with a solution of corrosive sublimate, lightly pressed into it, and then through a tube filled with chloride of calcium; the spot where the little strip of glass is lying is then heated to redness, whereby the arsenic is reduced, and is deposited in the usual manner.

Should the precipitated sulphuret of arsenic be in greater quan-

* Das Arsenik, seine Erkennung und sein vermeintliches Vorkommen in organisirten Körpern. Von Dr. A. Duflos und A. G. Hirsch. Breslau, 1842.

tity, 1 or 2 grs. for instance, it is dissolved in a warm dilute solution of caustic potash, and a quantity of nitric acid equal to the potash contained in the solution added, the whole dried, and the residue fused; it is then dissolved in water, saturated with acetic acid, boiled to expel the carbonic acid, precipitated with lime water, and the arseniate of lime collected on a filter, and mixed, while still moist, with 4 times its weight of a coarsely-powdered mixture of borax and charcoal, which has been previously heated to redness, then placed in a sublimation tube, and heated by the blowpipe-flame until the arsenic is reduced.

The following are the conclusions they draw from their researches:—

1st. Arsenic exhibits in its metallic state such characteristics as are fully sufficient to demonstrate that it is arsenic.

2nd. For this purpose the most trifling quantity is required, a quantity so small as to be almost imponderable.

3rd. The reduction of the arsenic therefore to its metallic state is absolutely necessary in medico-legal researches, in order to prove that the tested mass contains arsenic.

4th. The action of other reagents, however it may agree with the general characteristics of arsenious acid, can never be such as to render the reduction unnecessary.

5th. When the examination for arsenic is undertaken directly with organic substances, the test of Marsh requires many precautions and the greatest care. The process with sulphuretted hydrogen above described is therefore better and more certain.

6th. If Marsh's test be used, the best method of reducing the metal from the arseniuretted hydrogen is that of Berzelius, by means of oxide of copper (*Jahresbericht*, 1840, S. 193–198).

7th. By boiling with hydrochloric acid, all the arsenic is extracted; the tedious preparation with caustic potash or nitric acid is therefore unnecessary.

8th. Sulphuretted hydrogen precipitates the *whole* of the arsenious acid dissolved in the hydrochloric acid, in the form of sulphuret of arsenic.

9th. The reduction of arsenic from its combination with sulphur, according to the method long ago proposed by Berzelius, should be preferred to Marsh's test, and zinc perfectly free from arsenic is not even necessary.

10th. The treatment with nitric acid by Orfila's method is difficult and uncertain.

11th. Bones in their normal state contain no arsenic.

12th. The arsenic received into the organization of a living body does not remain, but is gradually expelled from it, unless life become extinct.—Berzelius's *Jahresbericht*, xxiii.

On the Determination of Copper.

M. Levol has suggested an important improvement in M. Fuch's method of determining copper in a solution of a copper salt, by

means of the quantity of copper which is dissolved in order to reduce it to the state of a protosalt. He conveys the solution of the salt into a flask, adds ammonia until the liquid is of a transparent blue colour, then fills the flask with boiling water, introduces a bright, well-cleansed slip of copper and closes hermetically. When the liquid has become colourless the slip of copper is removed, washed, dried and weighed. This method has the advantage of being applicable to all the persalts of copper, whatever the acid, and even with nitric acid.—Berzelius's *Jahresbericht* for 1842.

New Method of ascertaining the Specific Gravity of Fluids.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,

I notice your remarks relative to the communication you have received from Sir James Murray, wherein he claims being the first inventor and publisher of the instrument for ascertaining the specific gravity of fluids, which I forwarded for insertion in the Chemical Gazette.

In reply I beg to say, that in consideration of Sir J. Murray's having been the first to publish a description of an instrument of *similar principle*,—the accompanying extract, which is from the 'Mechanics' Magazine' of the 13th January 1844, being the only notice I have ever seen of it,—I am quite willing to accede to him whatever credit it may be entitled to: but for the additions and arrangement, as shown in your 33rd Number, which not only facilitate its use but ensure its accuracy in practice, I must be allowed to contest; and at the same time, in justice to myself, beg distinctly to affirm, that the *whole of the instrument*, as represented in your 33rd Number, page 125, was devised and a plan of it drawn in *June* last. This I can readily support by private testimony if required: the only reason I had for delaying its publication was, that at that time I had some intention of "registering" it under the new Design Act.

I am, Sir,

Yours very respectfully,

Norwich, March 19, 1844. F. HAM.

Extract from the Mechanics' Magazine.

"At the meeting of the Literary and Philosophical Society of Liverpool, Dr. Jeffreys called the attention of the Society to a new mode, proposed by Sir James Murray, at the Surgical Society of Ireland, of ascertaining the specific gravity of fluids. Sir James considered the common methods tedious and uncertain, owing to the inaccuracy of the balances generally used; he therefore proposed to let the atmosphere take the place of scales and weights, and exhibited a model of an apparatus, which consisted of two glass tubes, open at the bottom, and connected at the top by a shorter semicircular tube, or by a globe, so as to make the entire as it were one tube. The

cross-tube or globe was to have a stop-cock connected with it, by means of which, when the lower extremities of the tubes were inserted in two liquids, a portion of the air was to be extracted from the upper part of the tubes. In proportion as the air was rarefied the liquids rose in the tubes, and the height to which they rose was always in an equivalent to the specific gravity of each."

PHARMACOLOGY.

On Cortex Esenbeckiæ febrifugæ *and its bitter Substance.* *By* F. L. Winckler.

The bark examined by the author was brought to Europe along with *Cinchona de Rio Janeiro*, under the name of *Cortex adstringens Brasiliensis*; it agreed entirely with the descriptions given by Martius and Nees von Esenbeck. This bark is derived, according to Martius, from *Diosmia*; it not only resembles externally *Cinchona Piton*, which is generally ascribed to an *Exostemma*, being only somewhat lighter and smoother, but it also contains kinova bitter*. In the first experiments the author did not succeed in obtaining the bitter substance perfectly pure; and it moreover behaved totally different towards lime, to the kinova bitter from *Cinchona nova*; resembling in this respect the bitter substance from *Cinchona Piton*. On this account Buchner was inclined to doubt the identity of the two substances; but Winckler has ascertained, on continuing his experiments, that the substance extracted from the bark by æther, and decolorized with animal charcoal, is pure kinova bitter, and affords with oxide of copper and oxide of lead the characteristic combinations. If we extract the bark with alcohol, and treat the extract *a* with charcoal, *b* with charcoal and oxide of lead, *c* with lime, we then obtain three substances, of which only the first dissolves entirely in water, the third scarcely at all. What remains undissolved in the water is yellowish-white, resinous, bitter, insoluble in dilute sulphuric acid, and but very slightly in ammonia. Æther extracts from it pure kinova bitter, and leaves undissolved a reddish-brown substance. The aqueous solution affords with hydrochloric acid a yellowish-brown resinous precipitate; and the filtered solution, which has no longer a bitter taste, only affords chloride of potassium on evaporation. The substance soluble in water was the quinate of potash existing in the bark.

Both the cold infusion, as well as the decoction of the bark of *Esenbeckia*, is reddish-brown, froths on shaking, has a disagreeable and very bitter taste, and smells slightly of tannine; it is not precipitated immediately by a solution of gelatine, but after twenty-four hours an inconsiderable flocculent deposit takes place; with tannine it immediately affords a considerable dirty brownish-yellow precipitate, which is coloured dark greenish-brown by perchloride

* For an account of the preparation and composition of this substance, see vol. i. p. 15.

iron, and is scarcely altered by tartar-emetic and oxalate of ammonia; iodic acid causes in it a slight precipitate, and sulphate of copper affords an abundant dark greenish-brown deposit after a long time only.—Buch. *Rep.*, xxxi. p. 15–66 and 332–338.

Cinchona Pitoya

M. Muratori states that he has found in 12 ounces of this bark 17 grs. of quinine, 80 grs. cinchonine, 18 grs. of a peculiar substance, 3 drs. 24 grs. tannin, 33 drs. 36 grs. cinchona red, 1 dr. 8 grs. quinate of lime and quinic acid, 7 drs. gum, and 6 oz. 1 dr. 21 grs. woody fibre. This would prove that the *Cinchona Pitoya* of the Italians is a true Cinchona; also that it is very different from the bark known under that name in Germany, France, and England.—Buch. *Rep.* 31. p. 338.

CHEMICAL PREPARATIONS.

Infusum Sennæ Frigidum.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,

I HAVE lately been engaged in prosecuting some experiments with various preparations of senna, in the hope of discovering a more convenient form for administering it, and preserving unimpaired its medicinal properties, than that of the *Infus. sennæ comp.* at present employed; and I am induced to submit to your notice the conclusions I have arrived at, that through the medium of your Gazette some of your numerous readers may be enabled to avail themselves of the suggestions they afford.

It is commonly objected to the use of senna, that it invariably causes *tormina* or griping. It is to this well-known defect that I would now more particularly direct your attention, and I hope to be able to show that it is entirely the result of certain chemical changes which the infusion, as usually prepared, is very liable to undergo; and moreover I am of opinion that so long as the soluble substances are held exactly in the same state of combination as existed in the leaves, *tormina* will not be produced. But the true cause is undoubtedly to be sought for in the oxygen of the atmosphere combining with a portion of the albuminous matter which is always present, converting it into a body whose atoms are in a state of transposition, which in its turn will act as a nitrogenized ferment, and excite similar changes among the other ingredients, the amount of heat employed appearing to exert a decided influence over this disturbance, for the cold infusion will keep much longer than that made with hot water; but if a small quantity of it be retained only for a short time at the temperature of 212°, a separation of albuminous matter takes place, and then it passes quite as readily into a state of decomposition.

My endeavour therefore has been completely to prevent the occurrence of these changes, or at least to arrest them in their earliest stage; and the plan I have to recommend for this purpose is one which I have found very successful, and at the same time attended with but little trouble. It is as follows:—

Take 7½ oz. of *Fol. sennæ Alex.*, pack them carefully in any apparatus usually made use of in preparing infusions by displacement, pour upon them 23 oz. of cold distilled water, and macerate in a cool place for 10 hours, frequently drawing off from the bottom, and replacing at the top of the apparatus about 3 or 4 oz. of the liquid. At the end of that time the leaves must be submitted to powerful pressure, when 18 oz. of a dark-coloured infusion of 1045 spec. grav. should be procured; this must be mixed immediately with 2 oz. of *Sp. Vini rect.*, and after the precipitate which it produces has somewhat subsided, the whole must be filtered through paper.

A cold infusion made in this manner, if no delay be allowed in adding the spirit, will keep for a great length of time at ordinary temperatures, without the slightest appreciable disengagement of gas, or discernible change in smell or taste; a slight deposition of gummy matter is slowly formed, which I have ascertained to be unattended by any absorption of oxygen, the precipitate being quite inert, and generally adhering so firmly to the sides of the vessel in which it is kept as not to interfere with the transparency of the infusion. With respect to the dose of it, 2 fluid drachms will be found equivalent to 1 oz. of the *Infus. sennæ comp.* of the London Pharmacopœia. 500 grs. of it, evaporated very carefully at a gentle heat until they ceased to lose weight, left 8·5 per cent. of solid extract, whereas an equal weight of the common infusion gave 3·6 per cent. In estimating however the strength of these two preparations, by comparing the amount of solid matter left after each evaporation, some allowance must be made for the quantity removed during the filtration of the infusion; and I think you will admit, that in this, as in all similar questions relating to the doses of medicines, experience, together with an attentive consideration of the varied circumstances of each individual case, are alone to be relied on as our best and surest guides.

Faversham, Kent, Jan. 13, 1844. EDWARD LUND.

On the formation of Hydrocyanic Acid in the preparation of sweet Spirits of Nitre. By JOHN DALPIAZ.

The author having had occasion to prepare some sweet spirits of nitre according to the proportions prescribed by the London Pharmacopœia, found that the product gave with nitrate of silver a flocculent white precipitate, which presented all the characters of the cyanide of that metal. The formation of hydrocyanic acid under these circumstances is an interesting fact, and M. Dalpiaz resolved to investigate the influence which various proportions of acid and alcohol might have on this phænomenon at a temperature more or less elevated.

He distilled in the water-bath a mixture of—

Alcohol of spec. grav. 0·848	360 grms.
Distilled water.....	180 ...
Nitric acid of spec. grav. 1·35.....	90 ...

The products were received separately in five different portions, all afforded a precipitate with nitrate of silver, which weighed altogether 0·65 grm.

A fresh mixture of alcohol of sp. gr. 0·829..	100 grms.
Nitric acid of spec. grav. 1·35	100 ...

was heated very slowly in a large retort. It had scarcely boiled two minutes, without the solution of nitrate of silver, in which the products were received, presenting the least opacity, when all at once so large a quantity of hydrocyanic acid was disengaged that the liquid became in a moment thick and milky. Unfortunately, a few instants after the retort burst, and diffused vapours so strongly charged with hydrocyanic acid, that the author was obliged to quit the laboratory. This experiment not having afforded a definite result, it was repeated, the retort being sprinkled with cold water during the operation, in order to moderate the action. This time the amount of hydrocyanic acid disengaged was very small, and it is probable that none would have been formed had the reaction been slower. The elevation of temperature is therefore favourable to the production of hydrocyanic acid.

M. Dalpiaz concludes his note by observing that he had very seldom succeeded in detecting hydrocyanic acid in the nitrous æthers of commerce, but he always found in them a considerable amount of formic acid.

MM. Bernard de Rosne and Chatin have repeated and extended the above experiments. They find that hydrocyanic acid is produced in considerable quantity during the reaction of nitric acid on the fatty bodies. They have also confirmed the statement, that not the least trace of a cyanogen compound is formed when one portion of alcohol is distilled very carefully with two portions of nitric acid.

The formation of hydrocyanic acid during the reaction of nitric acid on certain organic substances is not a new fact. M. Gauthier de Claubry in 1839 demonstrated the presence of hydrocyanic acid in the alcohol obtained in the preparation of the fulminates; and last year M. Sobrero showed that it was likewise formed when nitric acid was distilled with the essential oil of beech and with various volatile oils, and even with several resins*. Long since M. Thenard announced that this acid was one of the products resulting from the action of nitric acid on sugar, gum, &c. Nevertheless the precise observations of M. Dalpiaz are of considerable interest. —*Journ. de Pharm.* for March 1844.

* See vol. i. p. 229.

On the preparation of Tannine. By M. Dominé.

The author, after detailing a series of experiments performed in the laboratory of M. Soubeiran, with a view to ascertain the best process for obtaining the above substance, recommends the following as being the most constant and the most productive:—

Expose the powdered galls in a cellar, and allow them to absorb *moisture from the atmosphere for three or four days*; convey them into a wide-mouthed vessel, which can be closed hermetically; a quantity of ordinary æther of 0·76 spec. grav. is poured over the galls, so as to form a soft paste. It is well mixed, which should be done very quickly by means of a wooden spatula, and the vessel closed. After four and twenty hours the substance is placed on a square piece of strong linen, and quickly subjected to the gradual action of a good press. The syrupy liquid which escapes is spread upon plates by means of a brush, which are then conveyed into a warm chamber, heated to from 104° to 113°. The substance swells considerably, and leaves the tannine in light laminæ, scarcely coloured.

The pressed mass is divided, placed in a vessel, and formed into a paste with æther charged with water. For this purpose, 100 of ordinary æther of 0·76 spec. grav. are violently agitated with 6 parts of water. Without allowing the two liquids time to separate, they are poured over the galls, and the operation repeated as above. Two such treatments suffice; a third only becomes necessary in case the press was not sufficiently powerful.

The tannine obtained by the process of M. Pelouze is not perfectly pure. According to the analysis of M. Guibourt, it retains a small quantity of chlorophylle, volatile oil, gallic and ellagic acids. The tannine obtained by pressure is probably still less pure, but it suffices for all medical purposes. To purify it, the following process, given by M. Guibourt, may be employed with advantage:— Equal portions of tannine, water and washed æther are introduced into a vessel and agitated for some time; the matter separates into three layers; the inferior one is pure tannine, which is then removed and dried in the usual way.—*Journ. de Pharm.* for March 1844.

New mode of preparing Chalybeate Wine. By E. Soubeiran.

In acting upon iron-filings with white wine, as the quantity of iron which is dissolved is in direct proportion to the acid principle of the wine, it is extremely variable. This evil is increased in Parmentier's formula, which consists in adding white wine to the tincture of the tartrate of iron, because the latter preparation never contains constant quantities of iron.

If the following formula be used, this defect is remedied; at the same time the wine may be prepared when required for use, and in as small a quantity as is desired. Take of the

Tartrate of the protoxide of iron.....	16 grs.
Tartaric acid.....	16 ...
White wine	1½ pint.

Triturate the tartrate and tartaric acid in a porcelain or glass mortar, then add the wine, and filter if necessary.

To avoid the alteration of colour produced in the wine by the iron, M. Béral recommends that it be previously shaken with a little hydrated peroxide of iron, then filtered, and allowed to act upon the filings; but in using, as I do, white wine of Bordeaux, the alteration of colour, whether the oxide of iron is used or not, is so slight as not to require notice.

The tartrate of protoxide of iron is made by decomposing an equiv. of protosulphate of iron by one of neutral tartrate of potash, quickly washing the precipitate with boiling water, collecting it on a linen cloth, strongly pressing, and drying it on a salt-water bath.—*Journ. de Pharm.* for March 1844.

[It is a valuable practice to add a portion of tartaric acid or bitartrate of potash to *antimonial wine* (*Vin. ant. pot. tart.*, P. L.), so as to retain the oxide of antimony in solution, or prevent its precipitation by any of the matters contained in the sherry wine.—Ed. *Chem. Gaz.*]

Veratrine Ointment and Acetate of Veratrine.

Veratrine made into an ointment with lard (3–10 parts of veratrine to 400 parts lard) has been used for many years by Calvé and other physicians at Montpellier, with the best effects in all forms of neuralgia. Sauvan, the apothecary, remarked that an ointment of veratrine, prepared with rancid fat, was more potent, and attributed this to the soluble (*acetate*) *salt* of veratrine which was formed by the liberated acid. The veratrine is dissolved by the acetic acid; at the same time a small quantity of an oily substance, which is coloured reddish-brown by nitric acid, is separated; and on evaporation a gummy, readily soluble salt, of a slightly bitter taste, is obtained, but more powerful than the pure veratrine which has been treated with æther. It will consequently be better to make the ointment of *acetate of veratrine and fresh lard* in small quantity, than to trust to the uncertain effect of the rancid fat.—*Pharm. Central. Blatt.*, Jan. 31, 1844.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Composition of the Gases produced in Metallurgical Operations. By M. Ebelmen*.

In the essay which I have the honour to submit to the Academy, I have continued the analyses of the gaseous products resulting in the operations connected with the treatment of iron, in order to de-

* An account of the author's former researches on this subject appeared at p. 468. vol. i. of this Journal.

duce either the calorific value of these gases, or the theoretical explanation of the phænomena which occur in the metallurgical apparatus. I have investigated, under this double point of view, the English method of treating iron, *i. e.* the manufacture of cast iron with coke, and the refining of the cast iron with coal in a reverberatory furnace.

I constructed, on two blast coke furnaces, those of Vienne and of Pont l'Eveque (Isere), in which coke is consumed, a similar arrangement to that which I described two years ago, relative to the two blast furnaces of Clerval and of Audincourt, which are heated with charcoal. I examined the variations which the composition of the gaseous column undergoes in ascending to the different points of height of the furnace, and have compared the results of these experiments with each other, and with those before obtained in the charcoal furnaces. The principal conclusions to which I have arrived are as follows :—

In the region of the furnace, comprised between the tuyère and the belly of the furnace, the gases generated with charcoal and with coke are identical in composition. In the two cases, the carbonic acid, the first produce of the combustion, is rapidly converted into carbonic oxide at a short distance from the tuyère, and the mixture of carbonic oxide and of nitrogen produced reaches the belly of the furnace, without undergoing any notable variations in its composition.

The analyses prove that the reduction of the oxide of iron of the ores to the metallic state is almost entirely effected in the fire-room, by the partial transformation of the carbonic oxide into carbonic acid without any consumption of charcoal. This result fully confirms the theoretical conclusions of my first essay. In the blast charcoal furnaces the zone of reduction is situated within the inferior half of the fire-room. With coke furnaces, on the contrary, it is in the upper part of the fire-room that the reduction takes place with the greatest energy.

The proportion of hydrogen, which varied from 2 to 6 per cent. from the base of the fire-room to the mouth in the charcoal furnaces, remains constant with the coke throughout the entire height of the furnace. This fact is easily explained by the difference in composition of the two combustibles.

The presence of sulphuret of iron in the coke induced me to look for the sulphur, isolated or in combination, in the gases of the blast furnace. I found no perceptible traces of it. All the sulphur is found in the fused metal or in the slag in the state of sulphuret of calcium, as M. Berthier has shown.

In order to explain the differences in the situation of the reductive zone, according as coke or charcoal is employed, I was induced to compare the temperature of the furnaces of Audincourt and Pont l'Eveque in parts of the apparatus similarly situated. I introduced metals, unequally fusible, into the furnace at different heights, in such a way as to ascertain two limits between which the temperature was comprised. I thus learnt that the temperature of the

blast coke furnaces was always remarkably more elevated than that of the corresponding parts of the charcoal furnaces. If the reduction of the oxide of iron begins with energy, quite near the mouth, in the coke furnaces, it is because the temperature of the gases at their exit is still very high, whilst it often sinks more than 100° in the charcoal furnaces.

These differences of temperature between the two classes of furnaces may be explained by this fact, that on an average twice as much carbon is consumed in the coke furnace as in that fed with charcoal, to obtain the same weight of a similar kind of fused metal.

In the furnace in which the metal is again melted for the mouldings, an inverse result is found. Twice as much charcoal as of coke is needed to remelt the same quantity of cast iron.

I have endeavoured to show to what causes these singular differences between the calorific effects produced by the two kinds of fuel in the furnaces of which I have just spoken are to be attributed, as well as in other furnaces employed in the arts. The explanation which I propose seems to apply to all cases. It is founded upon well-demonstrated differences in the relative combustibility of the two kinds of fuel, and on the results deduced from the experiments of Dulong on the heat of combustion of carbon and of carbonic oxide.

Dulong having also determined the heat of combustion of iron, I have been able, by means of the results of this illustrious chemist, and by means of the facts recognised relative to the composition of the gaseous products in the blast furnace, to arrive at a simple and rational explanation of several very remarkable phænomena which they present, and the cause of which had remained unknown up to the present time.

I have also determined, from the results of analyses, the quantities of heat which the combustion of gases might produce, their total volume, and the temperature of combustion. I thus recognised that the coefficient representing the lost heat was represented in the two coke furnaces investigated by the fractions 0·815 and 0·835, the total heat produced by the combustion of the coal being represented by unit; in the charcoal furnace of Audincourt this coefficient was 0·670.

The composition of the gases of the coke furnaces, the absence of sulphur in them, and the enormous quantities of heat developed by their combustion in the coke furnaces, which generally produce daily from 10,000 to 12,000 kilogrammes of cast iron, leave no doubt but that their employment will lead to important results. M. V. Frerejean, the able director of the foundries of Pont l'Eveque, in burning the gases of his blast furnace by processes identical with those employed at Vasseralfingen by M. Faber Dufaur, has succeeded in using them for feeding one of Mazerie's reverberatory furnaces, which has been in regular working for nearly a year.

I have also examined the composition of the air of the chimneys of furnaces for puddling and reheating. The manner in which the combustion takes place on the grating of the reverberatory furnaces of high temperature was not well known up to the present

time; and most founders supposed that the quantity of air not altered by its passage across the grating amounted generally to half of the total quantity. My experiments prove that this view is without foundation, and that the proportion of air not burnt in traversing the fuel, amounts on an average barely to six or eight-hundredths of the total quantity. When the excess of air sinks below this, very remarkable proportions of combustible gases are found in the chimney; the maximum of temperature of the forge corresponds to an excess of air of 5 to 10 per cent. in the gases of the chimneys. This result approaches very near to the theoretical data, according to which this maximum would correspond to the reciprocal and complete transformation of the air and of the fuel into water, carbonic and nitric acids.

I have also noticed the results of some new experiments on the transformation of solid combustibles into gas. Coke burnt in a forge having a fire-room, by a current of forced air, produced a gas formed of carbonic oxide and of nitrogen, the combustion of which allowed a reverberatory furnace to be kept at the necessary heat for the fusion of cast iron for several days. The analyses of the generated gases enabled me to discover an interesting fact, viz. the presence of a considerable proportion of sulphuretted hydrogen, a result which can only be attributed to the reaction of the aqueous vapour contained in the air projected on the sulphuret of iron of the coke.

The memoirs which I had the honour of submitting to the Academy on two previous occasions, respecting the transformation of combustibles into gas, have induced the proprietors of the works at Audincourt to adopt similar processes in their works, which have proved to be wholly practicable. Three generators of gas, consuming small coal of scarcely any value, are kept in constant and regular operation in these works. One of them feeds a furnace for sheet iron, which for five months has allowed of 30,000 kilogrms. of fine sheet iron being manufactured a month. In the other two, a white heat is obtained for soldering in the manufacture of coarse sheet iron, with the daily production of from 3500 to 4000 kilogrms. on an average for each furnace.

There is every reason to believe that similar processes to those employed at Audincourt will allow of earthy combustibles and those of bad quality being turned to account for the production of the highest temperatures required in the metallurgy of iron.—*Comptes Rendus*, March 4, 1844.

On the Extraction of Indigo from Polygonum tinctorium.
By M. Gaudry.

For some time chemists have been engaged in the extraction of indigo from various plants, and especially from *Polygonum tinctorium*. This plant is, in my opinion, the one from which the best results may be expected, both on account of its easy cultivation in our climate, and of the quantity and quality of the product.

From some previous experiments it appeared that the blue substance extracted from this plant was accompanied by some resinous principle, which seriously affects its properties. I have endeavoured to deprive the colouring substance of the resinous principle, but I could only succeed at a great expense, except on employing a process different from that generally in use, and which is at the same time simple and easy of execution. It is as follows:—

I took some leaves of the *Polygonum* before the flowering, piled them in heaps, and added for every 500 grms. 48 grms. of protosulphate of iron and sufficient water to cover the mixture, and subsequently a slight excess of subcarbonate of potash. The whole was then brought on to a filter, and the product received in water slightly acidulated with nitric acid, just sufficient to render the filtered solution faintly acid.

This excess of acid was then saturated with subcarbonate of potash, when the green liquid became blue, and afforded a precipitate. After twenty-four hours the liquid was decanted and the precipitate washed several times.

The indigo obtained in this manner has the property of dissolving in sulphuric acid, like that extracted from the various species of *Indigofera.—Journ. de Pharm.* for Feb.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Jan. 15, 1844. (The President in the Chair.) "On the Heat disengaged in Combinations."—Part II. By T. Graham, Esq.

The solution of sulphate of magnesia in water containing an equivalent of nitric and hydrochloric acids is attended with the same fall of temperature, and that twice as great as in pure water. The solutions of other sulphates, chlorides and nitrates in acids was also examined, and found to indicate various combinations and decompositions occurring on mixture. No perceptible change of temperature occurred in the formation of a double sulphate of magnesia and potash, nor of alum. In the formation however of a double salt which is more soluble than its constituents, such as sal-alembroth, there is a sensible disengagement of heat.

The heat disengaged in the neutralization of bichromate of potash by hydrate of potash is 8·96 degrees Fahr., in the neutralization of acetic acid 10·34 degrees, of oxalic 10·48 degrees. The heat disengaged in the formation of binoxalate of potash is 8·28 degrees; in saturating the acid of that salt 12·40 degrees; in the formation of quadroxalate of potash 10·56 degrees. The heat from the addition of a single equivalent of hydrate of potash to arsenic acid is 10·20 degrees, to phosphoric acid 10·00 degrees. In the progressive neutralization of each of these acids, which are tribasic, by three equivalents of

hydrate of potash, the proportion of heat evolved by the different equivalents of alkali was as follows:—

	Arsenic acid.	Phosphoric acid.
	°	°
By first KO	10·20	10·00
By second KO	8·10	8·08
By third KO	5·88	7·54
	24·18	25·62

"Note on a Means of preserving the Crystals of Salts as permanent Objects for the Microscope," by Robert Warington.

In some investigations of crystals by polarized light under the microscope, it was found by the author to be necessary to render these permanent, so that the same individual crystal could be re-examined, the investigation continued, and additional observations made. This was the more desirable from the extreme difficulty of obtaining perfect and isolated subjects, and the rapidity with which many of these undergo alteration by exposure to the air. The best medium for this purpose, after several trials, was found to be castor oil which had been filtered cold, and which did not deposit stearine or solid matter when submitted to a low temperature. The salt, when obtained fit for the observer's purpose, is to be carefully covered with this medium, a piece of very thin glass superposed, the superfluous oil removed, and the edges covered with a varnish of shell-lac in spirits of wine. In this way a permanent cell is constructed, and the object may be preserved for any length of time.

REVIEWS.

A Manual of Electricity, Magnetism and Meteorology. By Dionysius Lardner. Vol. II. *Edited and completed by* Charles V. Walker.

The present volume, one of the series of Lardner's Cabinet Cyclopædia, completes the articles Electricity, Magnetism and Meteorology. Circumstances have occurred which have delayed the appearance of this second volume for some considerable length of time, and have rendered it necessary for the publishers to seek the assistance of Mr. C. V. Walker to complete it. This the reader will have little reason to regret, as it has enabled the editor to include in it the multitudinous and important discoveries which have been made within these last few years in these interesting branches of science, a task which has been executed with great assiduity and ability.

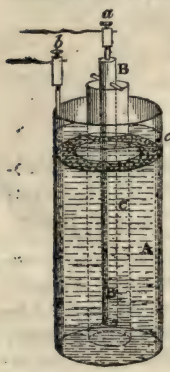
Of the several interesting applications of the science of electricity there is none perhaps of greater importance to the practical chemist than that of assaying by voltaic agency; we have therefore selected as an extract the chapter treating of this subject:—

"The application of electro-chemical action in assaying was practised many years ago by Mr. Martyn Roberts in the mining districts

of this country; M. Becquerel has long practised it in France. A quotation from Mr. Roberts, and another from M. Becquerel, will explain the two means of effecting this:—

"'If in an ore containing iron, copper, silver (metals whose affinities for oxygen stand in the order in which I have placed them), we wish to ascertain, first, the quantity of silver, and afterwards that of copper in the sample, dissolve the ore, and make a galvanic pair of silver as a negative, and copper as a positive plate; then immerse it in a measured quantity of the solution; the silver only is thrown down, because copper cannot throw down copper, and copper, as a positive plate, will not throw down iron, because the acid in which the ore is dissolved already holds the iron in solution with greater force than the affinity of the acid for copper—the positive pole. Having thus assayed for silver, into another measured portion of the ore in solution immerse a galvanic pair of iron as a positive plate, and either copper or silver as a negative, copper only is now thrown down, as iron cannot throw down iron.'

"Practically, for assaying copper ores, Mr. Roberts would now construct a single-cell apparatus of a cylinder of iron, and one of copper; the iron plate is in dilute muriatic acid, contained in the porous cell, and the copper plate in the surrounding solution of ore in nitro-muriatic acid; the gain of the copper in weight gives the value of the ore. M. Becquerel's mode of extracting gold from a mixed ore will illustrate his process generally:—



"'Let us commence upon a solution of gold and copper in *aqua regia*. The solution, which has been rendered as neutral as possible, is poured into the diaphragm, and this is placed in a vessel containing a solution of copper of the same degree of concentration, and in which a plate of copper is immersed; in the other is a plate of platinum; the two plates are placed in connection. The copper is immediately attacked, with the formation of protochloride; the electric current, which is developed, has an intensity sufficient to decompose the chloride of gold, and not the chloride of copper. . . . .

"'If we desire to extract the gold from a solution of lead, copper, iron and gold, a solution of the three former must be prepared in the same proportions, so as to have nearly the same density, and the experiment must be conducted as before, operating with a pair of platinum and copper. . . . .

"'To extract the copper without touching the other metals, the solution of the three metals must be replaced by another containing lead and iron. Thus, by operating with a pair of lead and platinum, or iron and platinum, the copper would be obtained.'

"These are both cases of *quantitative* analysis; one object of the French philosopher in using, to excite the positive element, a similar solution to the other, *minus* the metal to be extracted, is, that he may avoid the effect of endosmose—the passage of the liquid from

one cell to the other. The method of *qualitative* analysis practised by M. Becquerel, as early as 1823, is this:—

"'We may detect very small quantities of copper in gold, and even determine whether one specimen of gold contains more alloy than another: in fact, let us take a spoon of perfectly pure gold, and solder it to a platinum wire which is immersed into one of the mercury cups, in which the extremities of the wire of the galvanometer terminate; let us then place in a spoon some nitric acid, free from nitrous gas, and plunge in it the piece of gold, held in platinum nippers (connected with the other end of the galvanometric wire). Should the piece of gold contain copper, its action on the nitric acid determines a current from the gold spoon to the nippers,' &c.

"One more illustration of the influence of electro-chemistry in the arts of life, ere we close, unwillingly, this chapter:—

"'Tin, as we know, precipitates copper from its solutions; and nevertheless tin is precipitated from its solutions in the action of tinning pins. If the pins are introduced into a solution containing tin, a mixture of 1 part of subtartrate of potash, 2 of alum, 2 of sea-salt, and a certain quantity of water, the pins never become tinned, however long a time they may be left immersed in the solution; but if a *piece of tin* is placed in the solution so as to touch the pins, they are immediately tinned; the pins which are not touched by the tin are not tinned. To explain the effect produced, it must be remarked that the tin which is immersed suffers a feeble chemical action from the solution, in consequence of which the metal becomes negative and the solution positive; in making contact with the brass pins, they become the negative element of the voltaic pair, the energy of which is sufficient to determine the precipitation of the tin, which is, in common cases, easily reduced by the employment of the single pair.'"

The work is illustrated by five plates and numerous well-engraved woodcuts.

PATENT.

Patent granted to Frederick Steiner, *for a new manufacture of certain Colouring Matter, commonly called Garancine.*

The invention consists in manufacturing a certain colouring matter called garancine from refuse madder, or madder which has been previously used in dyeing, such madder having ordinarily been thrown away as spent and of no value, and the said colouring matter called garancine having been produced heretofore from fresh or unused madder. A large filter is constructed outside the building in which the dye-vessels are situated, formed by sinking a hole in the ground, and lining it at the bottom and sides with bricks without any mortar to unite them. A quantity of stones or gravel is placed upon the bricks, and over the stones or gravel common wrappering, such as is used for sacks. Below the bricks is a drain

to take off the water which passes through the filter. In a tub adjoining the filter is kept a quantity of dilute sulphuric acid, of about the specific gravity of 105, water being 100. Hydrochloric acid will answer the several purposes, but sulphuric acid is preferred as more œconomical. A channel is made from the dye-vessels to the filter. The madder which has been employed in dyeing is run from the dye-vessels to the filter; and while it is so running, such a portion of the dilute sulphuric acid is run in and mixed with it as changes the colour of the solution and the undissolved madder to an orange tint or hue. This acid precipitates the colouring matter which is held in solution, and prevents the undissolved madder from fermenting or otherwise decomposing. When the water has drained from the madder through the filter, the residuum is taken from off the filter and put into bags. The bags are then placed in a hydraulic press, to have as much water as possible expressed from their contents. In order to break the lumps which have been formed by compression, the madder or residuum is passed through a sieve. To 5 cwt. of madder in this state, placed in a wood or lead cistern, 1 cwt. of sulphuric acid of commerce is sprinkled on the madder through a lead vessel similar in form to the ordinary watering-can used by gardeners. An instrument like a garden spade or rake is next used, to work the madder about so as to mix it intimately with the acid. In this stage the madder is placed upon a perforated lead plate, which is fixed about five or six inches above the bottom of a vessel. Between this plate and the bottom of the vessel is introduced a current of steam by a pipe, so that it passes through the perforated plate and the madder which is upon it. During this process, which occupies from one to two hours, a substance is produced of a dark brown colour approaching to black. This substance is garancine and insoluble carbonized matter. When cool, it is placed upon a filter and washed with clear cold water until the water passes from it without an acid taste. It is then put into bags and pressed with a hydraulic press. The substance is dried in a stove and ground to a fine powder under ordinary madder stones, and afterwards passed through a sieve. In order to neutralize any acid that may remain, from 4 to 5 lbs. of dry carbonate of soda for every hundred weight of this substance is added and intimately mixed. The garancine in this state is ready for use.—Sealed August 8, 1843.

THE CHEMICAL GAZETTE.

No. XXXVI.—April 15, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Usnine or Usnic Acid, and its Occurrence in Lichens. *By* M. Knop.

We have already had occasion to announce, in noticing the results obtained by MM. Heldt and Rochleder (p. 160), that M. Knop was engaged in a more minute examination of this substance. He prepared it first from three species of *Usnea*, viz. *U. florida*, Hoffm., *U. hirta*, Hoffm., and *U. plicata*, Fries. It moreover occurs, according to Rochleder and Heldt, in *Parmelia fraxinea* and *farinacea*; further, according to the researches of the author, in almost all species of *Cladonia*, *e. g.* in *Cl. digitata*, *Cl. macilenta*, Fr., *Cl. uncinata*, &c.; further, in *Parmelia Hæmatomma*, Fr., *Biatora lucida*, Fr., *Lecidea geographica*, and in very large quantity in *Parmelia sarmentosa*, Ach.; and lastly, associated with another crystalline substance, in *Lecanora cruenta*, Ach. The sulphur-coloured and yellowish-green lichens are especially rich in usnine, for instance, *Lecidea geographica* and *Parmelia sarmentosa*. Usnine acts a conspicuous part by its various metamorphoses and combinations in the alterations of colour of many lichens. In all lichens however it is accompanied by yellow or green resins, which in common with it partake of the property of becoming red by ammonia and exposure to the air; this red colouring however is destroyed by sulphuretted hydrogen.

Usnine occurs in the thallus as well as in the fruit-discs. The shields of the *Cladoniæ* contain near the fruit-bearing vesicles quill-shaped cylindrical cells, which are coloured pale red at the base, but darker towards the apex by a colouring substance, which dissolves in ammonia and potash with a wine-red, in sulphuric acid with a carmine-red colour; the sulphatic solution is precipitated by water; the alkaline solution is not decolorized by sulphuretted hydrogen; properties therefore perfectly resembling those of an oxidized usnic acid. The nearly scarlet-red fruit-discs of the *Cladoniæ* become brown and blackish-brown with age. In fact, the fruit-discs of the lichens containing usnine are precisely similar in colour to the thallus, or brown, reddish-brown and carmine-red. With respect to the thallus, the usnine principally occurs, according to the researches of the author, in the bark layer; the medulla consists of quill-shaped and spherical cells: the former afford only a yellow extract with ammoniacal alcohol, the

latter contain a green resin soluble in æther. The sulphur-yellow lichens contain most usnic acid, and indeed in a free state; the other colours are probably produced by the action of the alkalies and earths of the vegetable salts in the lichens, the ammonia of the rain-water assisting the chemical action of the usnic acid, which is otherwise insoluble in water. In this manner the green, red and brown colours may originate. The silver-white *Cladonia rangiferina* probably contains the usnic acid in the state of an earthy salt. *Lecidea geographica* is sometimes sulphur-yellow, sometimes yellowish-green. If some pure yellow specimens be suspended in a glass over a solution of carbonate of ammonia, they become covered with carmine-red globules, after frequent washing entirely lose the usnic acid, and finally become grayish-white like dead lichens. The *Parmeliæ* and *Usneæ* continue of a brilliant green colour in shady and moist places, but when exposed to the heat of the sun they become brownish-black; if treated as above with ammonia and dried, they likewise present similar colours. The fruit-discs of the *Cladoniæ* also turn brown under similar treatment. The cause of all these changes is the usnic acid, which itself is of a yellow colour, but becomes oxidized in combination with bases by exposure to the air, forming various coloured compounds. Indeed the cortical layer of lichens appears very generally to contain substances which produce, with the subjacent layer of spherical cells filled with yellow and green resins, the colours of lichens. Thus the gray and whitish-gray thallus appears to contain colourless or white substances, which are able to absorb carbonate of ammonia from the atmosphere, and possess the property of weak acids, which produce by exposure to the air in combination with bases, coloured products of oxidation. However, these phænomena require more minute investigation.

The author obtained usnic acid by macerating for several days the cut lichens with æther at the ordinary temperature, removing the æther from the filtered product by distillation, adding some alcohol to the residue, and placing the mixture aside to cool. The usnic acid subsides in sulphur-yellow crystals, which need only be washed with a little hot alcohol.

Usnic acid crystallizes in sulphur-yellow prisms; the powder is of a brighter colour and very electrical. It melts at 392° to a yellow resinous liquid, which solidifies on cooling to a crystalline mass; at a higher temperature a portion sublimes unaltered, while another portion is decomposed, giving off suffocating vapours of a peculiar odour, and leaving a carbonaceous residue. It is insoluble in water, and like fat is not even moistened by it; it dissolves very sparingly in alcohol, slowly in cold, but readily in boiling æther, from which it always separates in sulphur-yellow crystals, even though it had previously been precipitated from a salt as a white powder.

Boiling oil of turpentine and fat oils likewise dissolve the usnic acid, from which it crystallizes on cooling in yellow prisms.

Usnic acid readily dissolves in concentrated alkalies, forming salts which are but little permanent, and are decomposed by all acids with the exception of carbonic acid. If the caustic alkali be in ex-

cess, the usnic acid is converted with access of air into a carmine-red body, which however is precipitated from the solution of a golden colour by acids. If the precipitate be melted, water escapes, and a carmine-red body is obtained, which dissolves in sulphuric acid with the same colour, but is thrown down from this solution by water of a yellow colour, redissolves however in potash of a red colour, and is not decolorized by sulphuretted hydrogen. With access of air and further action of potash, brown bodies are formed, which become gradually darker, and at last only a black tarry body is obtained on neutralization.

Ammonia produces the same changes, only more slowly.

Weak acids have no action upon usnic acid, nor has chlorine. Concentrated sulphuric acid dissolves it unchanged, and the solution affords, on being neutralized with carbonate of barytes, a mixture of sulphate and of usnate of barytes, from which the latter may be extracted by means of alcohol. Concentrated nitric acid destroys usnic acid on boiling.

The acid dried at 212° consisted of—

			Equiv.		Calculated.
Carbon	63·80	63·76	38 =	2854·5	63·90
Hydrogen	4·85	4·95	17 =	212·2	4·75
Oxygen			14 =	1400·0	31·35
				4466·7	

Usnate of potash is obtained by boiling a solution of carbonate of potash with an excess of the *pure* acid; it separates on cooling in scales of a silky lustre. If the acid contain resin, the salt crystallizes with great difficulty. It contains water of crystallization, which it parts with at the ordinary temperature, but entirely at 212°. Its solution becomes easily oxidized, forming the above-mentioned coloured products. The salt dried at 212° contains 11·06 per cent. potash; the formula $C^{38}H^{17}O^{14}KO$ requires 11·66.

Usnate of soda is very similar to the potash salt. On boiling its solution, it deposits yellow flakes of an acid salt.

Usnate of ammonia separates in crystals when ammoniacal gas is passed into a mixture of usnic acid and absolute alcohol. The salt is decomposed on boiling with water. When carbonate of ammonia is poured over pulverized usnic acid, it forms a compound which is insoluble in carbonate of ammonia, but soluble in water; it is likewise decomposed by boiling. Dry usnic acid absorbs ammoniacal gas and loses its yellow colour.

The *earthy* and *metallic* salts are obtained by double decomposition of the potash salt, which is the most permanent of all the usnates. They are almost all deposited in amorphous flakes, insoluble in water, which on heating mostly contract into crystalline granules. Alcohol dissolves those which contain water; æther extracts a portion of the usnic acid. The metallic salts generally afford with an excess of the precipitant, compounds which dissolve in hot water, but on cooling again separate in flocculent precipitates.

The *barytic salt* is first precipitated in an amorphous state, but is

converted on boiling into brilliant white scales. It contains water of crystallization, which it readily parts with at 212°. It dissolves in alcohol, but that which has been once dried, or crystallized from *strong* alcohol, does not dissolve in alcohol unless it has been previously digested for a considerable time in water, in which operation its colour generally begins to be altered. The salt dried at 212° contains 17·32 to 17·47 per cent. barytes; the formula $C^{38} H^{17} O^{14}$, BaO requires 17·66.

The *peroxide of copper salt* is a grass-green, highly electrical powder, of constant composition, if an excess of the precipitant has been avoided.

Dried at 212° it contained—

				Equiv.		Calculated.
Carbon	57·20			38	= 2854·5	57·5
Hydrogen	4·38			17	= 212·2	4·3
Oxygen				14	= 1400·0	28·2
Oxide of copper	10·20	10·28	10·43	1	= 495·7	10·0
					4962·4	

It is evident therefore, since every other calculation would afford numbers differing widely from the analytical results, that the usnic acid is in its free state anhydrous, and contains no basic water. It is however possible that it may contain this water under certain circumstances, but part with it as readily as other bases, on account of its very weak acid properties.—*Göttinger gelehrte Anzeigen*, 1843, 2 and 3 St., pp. 16–32.

Formation of Chloride of Nitrogen in the Preparation of Liquid Chloride of Tin.

M. Bechstein twice observed a very violent explosion in the preparation of liquid chloride of tin, by passing chlorine gas into a concentrated solution of the ordinary ammoniacal tin salt. Dœbereiner ascribes this to the formation of chloride of nitrogen, which always happens when the ammoniacal tin salt is treated with more chlorine gas than is requisite to convert the protochloride of tin into the perchloride.—*Archiv der Pharm.*, xxxiv. p. 288.

On the Products of Decomposition of Benzoate of Ammonia by Heat. By M. Fehling.

When benzoate of ammonia is evaporated to dryness, and heated in a retort provided with a refrigerator, a very voluminous and light sublimate is formed, which is pure benzoic acid; water and ammonia pass over. After a considerable length of time some drops of oil, having the peculiar odour of oil of bitter almonds, make their appearance in the recipient along with the drops of water. More of this oil is obtained on distilling the melted residue in the retort with water; this is again distilled to dryness, the residue heated to melting, more water added and some ammonia (which latter is scarcely necessary, as the water which passes over has always a strong ammoniacal odour); this mixture is again submitted to distillation.

The author obtained in this manner, in five days, from 12 oz. of benzoic acid, 6 oz. of impure oil. A large portion of the benzoic acid was reobtained unaltered from the sublimate and the residue; for the slightly-coloured residue afforded, when recrystallized from water and washed with a little alcohol and water, pure benzoate of ammonia (the analysis afforded 18·2 per cent. ammonia), from which acids precipitated pure benzoic acid.

The oil, which may be called benzonitril, and which is probably identical with that oil which the author formerly obtained accidentally on submitting a product from the action of peroxide of lead on hippuric acid, probably impure benzamid, to dry distillation*, was purified by washing with a little dilute muriatic or sulphuric acid and water, drying over chloride of calcium and redistillation. It is then clear and colourless, of a strong and agreeable odour of oil of bitter almonds; it is soluble in about 100 parts boiling water, in every proportion in æther and alcohol, and possesses a burning taste; it is heavier than cold water, lighter than hot; specific gravity at 57° = 1·0073. At 374° it begins to boil; the boiling point rises somewhat at first, but remains constant at 376°. It is inflammable, and burns with a luminous smoky flame. Its coefficient of refraction for light is, according to Reusch, 1·503. Potassium colours it brown, but only when heated with it; it is decomposed by the action of mineral acids and strong bases into benzoic acid and ammonia, with simultaneous decomposition of water. It afforded on analysis—

Carbon..	81·92	81·87	81·78	81·38	81·49	14=1062·00	81·60
Hydrogen	4·98	5·16	5·05	4·84	4·99	5= 62·40	4·79
Nitrogen	13·67	13·35		13·16	14·08	1= 177·04	13·61
	100·57	100·38		99·38	100·56	1301·44	100·00

The specific gravity of the vapour was found to be 3·7. Calculation affords—

$$\frac{14{\cdot}439}{4} = 3{\cdot}61.$$

Benzonitril is therefore isomeric with Laurent's nitrobenzoile; at its formation, which is quite analogous to that of prussic acid from formate of ammonia, and of cyanogen from oxalate of ammonia, $C^{14} H^5 O^3$, NH^3, affords simply $C^{14} H^5 N$ and 3HO. If acetate of ammonia behaved in an analogous manner, it would afford by heat a body composed of $C^4 H^3 N$.

Succinate and benzoate of ammonia, so similar in this respect that their solutions cannot be evaporated without loss of ammonia, differ when exposed to a high temperature; for the succinate of ammonia not only parts with water but likewise with ammonia, and affords the amidogen compound of the monobasic succinic acid, namely bisuccinamid. The difference is probably owing to benzoic acid being a monobasic, succinic acid a polybasic acid.—*Ann. der Chem. und Pharm.*, xlix. pp. 91–97.

* That oil likewise possessed the smell of oil of bitter almonds, and gave with manganese and sulphuric acid no benzoic acid, which was however the case on being treated with nitric acid.

On the Preparation of Iron-Alum.

M. Bolley observes, that frequently in preparing iron-alum the basic double salt of Maus $2SO^3$, $F^2O^3 + 2(SO^3, KO) + 6HO$ is obtained, which crystallizes in olive-green hexangular tablets and columns. It forms when the solutions are crystallized hot; the yellow cold solution of iron-alum becomes dark red on being warmed. It likewise appears as if the octahedrons of the iron-alum effloresce in the direct light of the sun, and are converted into that double salt. This decomposition results from the great tendency of the potash to form bisulphate, thereby rendering the peroxide of iron-salt basic. A large quantity of bisulphate of potash occurs in the mother-ley. The olive-coloured compound affords on boiling a still more basic yellow and insoluble salt. The latter contains variable quantities of potash-salt, but equal equivalents of sulphuric acid and peroxide of iron. The author has examined a pale green salt resembling green vitriol which had been deposited in the vessels of a chemical manufactory in which formerly iron-alum had been prepared, and which had been exposed to the atmosphere for many years. It contained 17 per cent. protoxide of iron, 24·4 water, 38·4 sulphuric acid, and 20·2 potash, therefore $= FeO, SO^3 + KO, SO^3 + 6HO$. This double salt might perhaps, on account of its greater stability, be employed instead of green vitriol in many cases where a deal depends on the constant amount of oxygen and water, as for instance in chlorometry.—*Jahrb. für Prakt. Pharm.*, vii. p. 235.

Extraction of the Colouring Substance from the Shell of the common Crab. By M. E. de Grote.

The beautiful red tint which the shell of a crab acquires on boiling is known to every one. To extract this colouring substance, the pulverized shell, dried by exposure to the air, is treated with caustic potash, and submitted to the action of heat until the liquid has assumed an orange colour; it is then filtered, an excess of hydrochloric acid added, and again heated. After a certain time the colouring substance separates in the form of dark red flakes. It is soluble in alcohol.—*Comptes Rendus*, March 11.

PHARMACOLOGY.

On the Derivation and Chemical Constitution of Cinchona californica. *By* F. L. Winckler.

The bark submitted to examination by the author was imported as *Cinchona nova*; it quite agrees with the description and figures given in Göbel's 'Pharmacologia.' The author could not detect among it any tube cascarilla-like pieces, as described by Batka; but

he has frequently found some cascarilla-like fragments of *Cinchona nova surinamensis* mixed with *Cinchona lima*. Batka derives the *Cinchona californica* from a *Portlandia*, Decandolle from *Buena obtusifolia*; but Geiger considers it identical with *Cinchona braziliensis*. The *Cinchona californica* is however decidedly distinct from the latter, from its containing, according to Rauch, no kinova bitter.

The cold aqueous infusion of the bark is of a light brownish-red; it is clear, has a slightly bitter taste, smells of tan, but has neither an acid nor an alkaline reaction; it is not altered by tannine, sesquichloride of mercury and tartar-emetic; it is rendered darker by perchloride of iron, and is first coloured darker by green vitriol, and subsequently precipitated of a dark dirty violet; sulphate of copper affords, after a long time, an inconsiderable brownish-red, finely-granular deposit; acetate of lead an abundant pale brownish-red precipitate; iodine and solution of gelatine give inconsiderable deposits after some length of time. The saturated aqueous decoction is brownish-red; it is tolerably clear on cooling, and froths on being shaken; the taste, odour and reactions are the same as with the infusion, with slight differences.

Æther extracts only a tasteless fatty matter from the bark; if it is then exhausted with alcohol, a bitter tincture is obtained, which is clear and of a dark reddish-brown colour by transmitted light, brownish-green by reflected light; it leaves on evaporation about 10 per cent. of the bark employed of a bitter brownish-red extract. This extract redissolves only partially in water; the undissolved portion is reddish-brown, amorphous, and soluble in alcohol of 80 per cent. The solution exhibits the same phænomena of colours; it is precipitated by water and by perchloride of iron. A bitter substance was separated from the aqueous solution of the extract by precipitation with acetate of lead, decolorizing the liquid freed from the excess of lead with animal charcoal, evaporation and re-solution in alcohol of 90 per cent., and then mixing the tincture with æther; it appeared when dry of a golden-yellow colour, is not crystalline, dissolves readily in alcohol and water with a golden-yellow colour, but not at all in æther, resembles salicine in taste, is not reddened by sulphuric acid, and is not precipitated from its aqueous solution either by tannine, chloride of platinum, perchloride of mercury, perchloride of iron, or neutral acetate of lead. It is therefore no alkaloid.

The author found, on further treatment of the bark, besides the above substance, to which he has applied the name of Californine, the fat and the resinous colouring substance resembling quina-red, gum, starch, malate of potash and fibre; potash also extracted a small quantity of a body resembling quina-red.—Buch. *Rep.*, xxxii. p. 20.

On Rad. Galangæ. *By* A. Vogel, Jun.

M. Buchholz found in *Rad. Galangæ* essential oil, a soft resin, extractive substance, gum and bassorine. The author found moreover

starch and a fat oil. Cold water extracts gum, chloride of calcium, chloride of potassium and gypsum; boiling water affords an extract which contains much starch, gives a green colour with persalts of iron, and which on evaporation leaves a brown horny residue. Boiling alcohol gives a yellow-brown tincture, which on evaporation leaves a soft residue, possessing the odour and taste of the root, which yields very little to water. Boiling æther produces a yellow solution, which on evaporation affords a brown extract and a yellow fat oil, in which some essential oil is dissolved. The fat oil may be separated by pressure between bibulous paper into a solid and a liquid portion.

On distilling the root with steam, a colourless essential oil is obtained, which dried, and dehydrated by means of chloride of calcium, consisted of—

Carbon	74·923	74·881
Hydrogen	11·557	11·548
Oxygen	13·520	13·571
	100·000	100·000

approaching therefore in its composition to cajuput oil.

The water separated from the essential oil is neutral, has the odour and taste of the root, and gives with acetate of lead a precipitate of carbonate of lead. Treated with muriatic acid and evaporated, it leaves a saline, entirely volatile residue, from which potash liberates ammonia. The water therefore contains carbonate of ammonia, the formation of which is probably owing to some nitrogenous body contained in the root.—Buch. *Repert.*, xxxiii. p. 19.

CHEMICAL PREPARATIONS.

On the Preparation of the Hydrated Peroxide of Iron and of Liquor ferri acetatis. *By* M. Trautwein.

According to the author it is requisite, in the preparation of *Liquor ferri acetatis*, that the liquids employed in the precipitation of the hydrated peroxide of iron should possess the requisite degree of dilution, and that an excess of acetic acid should be avoided for dissolving the hydrate. The various hydrates of the peroxide of iron are not always sufficiently distinguished; the hydrate $2Fe^2O^3+3HO$ is not the one that should be employed as an antidote against arsenic, nor in the preparation of the *Liquor ferri acetatis*, but the hydrate Fe^2O^3+3HO, which when well dried contains 27 per cent. water.

This hydrate is obtained by diluting 6 ʒ *Liq. ferri sesquichloridi* of 1·545 spec. grav. with 90 ʒ of distilled water, then adding 6 oz. of caustic potash of 1·333, diluted with 80 oz. of water, shaking until the precipitate formed has redissolved to a clear solution, and now precipitating by the careful addition of an equally dilute solution of potash. The brownish-red gelatinous precipitate is thrown on to a

strainer, and the chloride of potassium removed by washing; it is then reduced by pressure to within 3 to 6 oz., or in case it is to be preserved as an antidote, only to 12 oz. This residue is dissolved in $3\frac{1}{2}$ oz. of acetic acid of 1·05, so much water being added that the whole amount to 12 oz. The solution is poured through a piece of linen; it is perfectly clear, and contains one-twelfth iron. It is best to add immediately the amount of alcohol prescribed in preparing the tincture, and to preserve it in this state, adding the acetic æther on filling the shop bottles. The tincture so obtained contains one-sixteenth iron or one-twelfth oxide, and has a spec. grav. of 1·055 to 1·06. One drop imparts a beautiful wine-yellow colour to 2 oz. of water. It is not easily decomposed, and even on being heated only becomes transitorily thicker.

The author believes that the iron does not exist as oxide in Klaproth's tincture when it has been correctly prepared, but is in a state of hydrate, at least for two-thirds. The above-mentioned hydrated peroxide of iron dissolves readily in dilute acids, forming tribasic compounds, which on being heated generally decompose into the neutral salt and oxide, which is rendered immediately perceptible by an alteration of the colour from a dark reddish-brown to a yellowish-brown. Solutions which contain the hydrate afford a more voluminous precipitate with tannine than those containing the peroxide.—Buch. *Repert.*, xxxii. p. 1.

Observations on Quinovine. *By* M. Winckler.

The author has prepared this alkaloid from 104 oz. of light *Jean Cinchona*, according to Manzini's process*. The lime precipitate formed in the acid extracts was very voluminous, the alcoholic extract of an intense greenish-yellow colour; on evaporation, the crude alkaloid (6 drachms) was obtained in the form of a brownish-yellow, very bitter resin, the purification of which was rendered extremely difficult from the presence of a yellow resin, so that after dissolving in acetic acid, treatment with oxide of lead, basic acetate of lead and animal charcoal, precipitating the decolorized filtered solution by ammonia and re-crystallization from alcohol, only 60 grs. of pure alkaloid were obtained.

M. Winckler has found this alkaloid, upon a most careful comparison, to be identical with cusconine or aricine, nor do the analyses of the two differ very much. Manzini found in quinovine 69·92 C, 7·04 H, 7·39 N, and Pelletier in cusconine 70 C, 7 H, 8 N.—Buch. *Repert.*, xxxi. p. 249.

Preparation of Tartarus ammoniatus. *By* M. Veling.

To obtain a perfectly neutral salt in beautiful crystals, I prepare a highly-concentrated solution of pure bitartrate of potash with *Am-*

* See this Journal, vol. i. p. 45.

mon carb., add a slight excess of *Liquor ammon. caust.*, and pour over it twice the amount of highly-rectified alcohol, as in the preparation of *Cupr. sulph. ammon.*; close the vessel with moist bladder, and let it stand. If the salt is not wanted in crystals, it is only requisite to shake the alcohol with a saline solution. It causes much less trouble to reobtain the alcohol than to produce the preparation in the ordinary manner, without there being equal certainty of obtaining it perfectly free from every objection.—*Arch. der Pharm.*, Feb. 1844.

Employment of Succinate of Ammonia in the treatment of Delirium Tremens. By Dr. Scharn.

The resistance of the disease known by the name of delirium tremens to the numerous therapeutic agents employed for its removal is well known. The different kinds of antispasmodics and opiates have most frequently proved ineffectual against this violent disease. It would therefore be extremely desirable if the treatment prescribed by Dr. Scharn should prove more efficacious than those hitherto proposed.

This physician having learned the uselessness of the means generally employed, considered that this disease, being nothing less than drunkenness itself arrived at its highest degree, should be treated by the same means which prove successful against the latter, and that consequently ammonia should form a remedy. M. Scharn prescribed therefore succinate of ammonia in delirium tremens. By means of this simple remedy, he observed the most serious cases and the most furious delirium pass away as by magic in a few hours, without its being necessary to have recourse to any other agent.—*Journ. de Pharm.* for March 1844.

On Cathartine.

M. Herrlein has prepared the so-called cathartine from the leaves of senna, according to the method of Lassaigne and Feneulle*, and has found not only that it does not possess any purgative property, but that it is likewise of a more complex nature. It is dark brown, soft, amorphous, of a disagreeable smell, and possesses an acid, bitter, unpleasant taste; it is hygroscopic, dissolves in water and in alcohol, but not in æther; the aqueous solution has an acid reaction, is rendered darker by alkalies, but is not precipitated by them any more than by dilute acids; it affords no precipitate with tartar-emetic, sulphate of zinc, sulphate of copper, chloride of platinum and chloride of mercury; with tincture of iodine some iodine is separated; neutral and basic acetate of lead render it turbid, tincture of galls produces a dirty yellow precipitate, and it is rendered darker by protosulphate of iron. On ignition, cathartine leaves behind an alkaline ash.—Buch. *Repert.*, xxix. p. 219.

* See this Journal, vol. i. p. 242.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a Method of ascertaining whether a Pearlash has been adulterated with Soda, and of determining in a simple Manner the Proportion of the latter. *By* E. F. Anthon.

For commercial purposes, both the determination of the two bases in the state of chlorides, and the method of separation by means of perchloric acid, are inapplicable, from their requiring much time and considerable skill in chemical manipulation; nor can the commercial value of a pearlash be estimated from its capacity of saturation. The object of the author in undertaking the present investigation was to discover a process adapted to the wants of the merchant and manufacturer, for the easy detection and valuation of the amount of soda contained in commercial pearlash.

He found that it was possible to form an approximative estimation by converting the pearlash into bicarbonate, by passing carbonic acid through the solution, evaporating and treating the residue with a saturated solution of bicarbonate of soda, which dissolves the bicarbonate of potash and the other salts, leaving behind the bicarbonate of soda. However, the amount of soda always turns out too small, from its being extremely difficult to convert a mixed solution of carbonate of potash and carbonate of soda into bicarbonates.

Another method, which is likewise only approximative, is based on the fact that carbonate of potash combines with no water of crystallization, while carbonate of soda does; it is therefore possible to conclude how much soda is present, from the amount of water requisite to convert a definite quantity of calcined pearlash into a permanent pasty condition. The author's experiments gave the following results:—

90	parts potash and	10	of anhydrous soda require	17	water.
80	...	20	...	40	...
70	...	30	...	57	...
60	...	40	...	68	...
50	...	50	...	80	...
40	...	60	...	95	...
30	...	70	...	107	...
20	...	80	...	118	...
10	...	90	...	130	...

With respect to the exactitude of this process, it still leaves much to be desired; for according to the author, even when familiar with the mode of execution, it may give rise to an error of from 2 to 3 per cent. The impurities however which ordinarily occur in pearlash have scarcely any influence on the correctness of the result, these being generally substances, such as sulphate of potash, chloride of sodium, chloride of potassium, silica, &c., which do not combine with any water of crystallization. To persons unacquainted with chemistry it might suffice from its great simplicity.

The author finally arrived at the following process:—Two separate portions, each of 100 grs., of the pearlash under examination are weighed off; the one is submitted to the usual alkalimetrical test, the amount of the test acid consumed looked for in the first table, and the corresponding quantity of carbonate of potash noted down. The second 100 grs. are then dissolved in from 8 to 10 times the quantity of a solution of bitartrate of potash which has been perfectly saturated at the ordinary temperature, and of which a tolerable quantity should always be kept in readiness where such examinations are of frequent occurrence. The solution is filtered into a flask capable of holding about a pound of water, and the filter washed with a cold concentrated solution of the bitartrate; at present as much finely pulverized tartaric acid is added as is requisite (which is seen in the first table) to convert the whole of the alkali contained in the pearlash, whether it be potash or soda, or both, and whether it be either in the caustic state or in that of carbonate, exactly into the state of bitartrate. As soon as this is done, so much of the same solution of bitartrate is poured into the flask that the entire quantity amounts to about 6400 grs. An excess or deficiency of a small quantity is not of much importance. In order not to be obliged to weigh each time, the level to which the liquid reaches may be noted by a scratch of the file.

The flask is now closed, placed in a warm situation, and shaken frequently. It is not at all necessary that the bitartrate of potash already formed should entirely dissolve, because it does not prevent the alkali from being entirely converted into bitartrate and changed into a fine crystalline powder; but in order that subsequently the precipitation of the pulverulent bitartrate of potash should take place in a very uniform manner and allow of a careful admeasurement, it is best to warm the closed flask, and to agitate it until perfect solution has been effected. This however may be omitted without any danger of committing an essential error.

The warmed flask, kept closed, is now cooled as quickly as possible by immersion in water, or in snow if it be winter, and violently agitated the whole of the time. It is advantageous to lower the temperature of the flask and of its contents even below that of the surrounding atmosphere, so as to obtain a crystalline powder of a very equal grain; but it is requisite in this case subsequently to raise their temperature to the degree which the cold concentrated solution of the bitartrate possessed at the commencement of the experiment, which is easily effected. This being accomplished, the cork which closes the flask is replaced by another, into which is fitted the open extremity of the measuring tube*, taking care that neither the tube nor the cork descend into the neck of the flask more than is necessary for the cork to join firmly on to the sides of the neck, in order that on reverting the bottle none of the crystalline powder can get between the cork and the neck of the bottle. The flask is

* This is 3′ in length and 5‴ in diameter, and divided from the closed end into 100°, each of which corresponds to 1 gr. of carbonate of potash.

now turned upside down, shaken, and in this manner the whole of the powder transferred into the tube; the flask is then removed, and the tube knocked against some solid body until the crystalline powder has subsided into the smallest possible space, when the per-centage amount of pure carbonate of potash in the sample examined can be read off without any further operation.

Having learned, in the manner described, the quantity of pure carbonate of potash in the sample, we look for the difference which exists between the centesimal parts of test acid employed with the alkalimeter and the centesimal parts of carbonate of potash found in the measuring tube, which number is sought for in the second table, and indicates, without further calculation, the per-centage amount of soda with which the pearlash had been adulterated.

Let us suppose, for example, that 100 grs. of a pearlash required for their neutralization 60° of the test acid; we look in the first table for the corresponding quantity of carbonate of potash, which is found to be 87·5. Now if 100 grs. of the same potash likewise gave 87·5 parts of crystalline powder in the measuring tube, there would be no difference between the two numbers found, and we should conclude that the potash in question had not been sophisticated with soda.

If, in another experiment, the quantity of carbonate of potash found with the alkalimeter were 52, while the measuring tube indicated only 32, we should have to subtract this latter number (which represents the per-centage amount of pure carbonate of potash actually contained in the pearlash) from the first, and look for the difference (in this case 20) in the second table, in order to find the number of centesimal parts of soda with which the sample examined had been adulterated; in the present case this would be 22·5. The 25·5 hundredths still wanting should then be attributed to the ordinary and accidental impurities of the pearlash.

Or if a saline mass, sold for potash, indicated with the alkalimeter 80°, while on the contrary no crystalline powder was formed in the measuring tube, the salt in question would be nothing less than carbonate of soda, with 10 per cent. of other impurities.

In conclusion, it may be observed that this method is susceptible of further simplification, by employing an alkalimeter with a solution of tartaric acid saturated with bitartrate of potash in the place of test acid, and dividing the alkalimeter in such manner that each degree corresponds to 1 gr. of pure carbonate of pearlash; for in this case it suffices to neutralize the 100 grs. of potash submitted to examination, to note down the quantity of test acid employed, then to add an equal amount of test acid, and to proceed as above described; the difference between the carbonate of potash indicated on the alkalimeter and in the tube will give, by means of the second table, the extent of adulteration:—

Table 1.

Degrees of the alkalimeter.	Corresponding to the following quantities of carb. potash.	And requiring of tartaric acid.	Degrees of the alkalimeter.	Corresponding to the following quantities of carb. potash.	And requiring of tartaric acid.
1	1·43	3·19	46	67·08	147·07
2	2·91	6·39	47	68·54	150·27
3	4·37	9·59	48	70·00	153·47
4	5·83	12·78	49	71·45	156·67
5	7·39	15·98	50	72·91	159·86
6	8·74	19·18	51	74·37	163·06
7	10·20	22·38	52	75·83	166·26
8	11·66	25·57	53	77·29	169·46
9	13·12	28·77	54	78·75	172·65
10	14·58	31·97	55	80·20	175·85
11	16·04	35·17	56	81·66	179·05
12	17·50	38·36	57	83·12	182·25
13	18·95	41·56	58	84·58	185·44
14	20·41	44·76	59	86·04	188·64
15	21·87	47·96	60	87·50	191·84
16	23·33	51·15	61	88·95	195·03
17	24·79	54·35	62	90·41	198·23
18	26·24	57·55	63	91·87	201·43
19	27·70	60·75	64	93·33	204·63
20	29·16	63·94	65	94·79	207·83
21	30·62	67·14	66	96·25	211·02
22	32·08	70·34	67	97·70	214·22
23	33·54	73·53	68	99·16	217·42
24	35·00	76·73	69	100·62	220·61
25	36·45	79·93	70	102·08	223·81
26	37·91	83·13	71	103·54	227·01
27	39·37	86·32	72	105·00	230·21
28	40·83	89·52	73	106·45	233·40
29	42·29	92·72	74	107·91	236·60
30	43·75	95·92	75	109·37	239·80
31	45·20	99·11	76	110·83	243·00
32	46·66	102·31	77	112·29	246·19
33	48·12	105·51	78	113·75	249·39
34	49·58	108·71	79	115·20	252·59
35	51·04	111·90	80	116·66	255·79
36	52·50	115·10	81	118·12	258·98
37	50·95	118·30	82	119·58	262·18
38	55·41	121·50	83	121·04	265·38
39	56·87	124·69	84	122·50	268·57
40	58·33	127·89	85	123·95	271·77
41	59·79	131·09	86	125·41	274·97
42	61·25	134·28	87	126·87	278·17
43	62·70	137·48	88	128·33	281·36
44	64·16	140·68	89	129·79	284·56
45	65·62	143·88			

Table 2.

When the difference is	The potash is adulterated with	When the difference is	The potash is adulterated with
1	1·125 soda	46	51·75 soda
2	2·25	47	52·87
3	3·37	48	54·
4	4·50	49	55·12
5	5·6	50	56·25
6	6·75	51	57·37
7	7·87	52	58·5
8	9·	53	59·62
9	10·12	54	60·75
10	12·375	55	61·87
11	11·25	56	63·
12	13·5	57	64·12
13	14·62	58	65·25
14	15·75	59	66·37
15	16·87	60	67·5
16	18·	61	68·62
17	19·12	62	69·75
18	20·25	63	70·87
19	21·37	64	72·
20	22·50	65	73·12
21	23·62	66	74·25
22	24·75	67	75·37
23	25·87	68	76·50
24	27·	69	77·62
25	28·125	70	78·75
26	29·25	71	79·87
27	30·37	72	81·
28	31·5	73	82·12
29	32·62	74	83·25
30	33·75	75	84·37
31	34·87	76	85·50
32	36·0	77	86·62
33	37·125	78	87·75
34	38·25	79	88·87
35	39·37	80	90·
36	40·50	81	91·12
37	41·62	82	92·25
38	42·75	83	93·37
39	43·87	84	94·50
40	45·	85	95·62
41	46·12	86	96·75
42	47·25	87	97·87
43	48·37	88	99·
44	49·50	89	100·12
45	50·62		

Buchner's *Repert. der Pharm.*, xxxi. p. 1.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Feb. 5. (E. F. Teschemacher, Esq., in the Chair.) "Observations on the Green Teas of Commerce," by Robert Warington, Esq.

On submitting a sample of green tea, supposed to be spurious, and which had been seized by the Excise, to microscopic investigation, the author found that the variation of tints, which had led him to this mode of examination, was dependent on adventitious substances mechanically attached or dusted on the surface of the curled leaves. The principal part of this powder was of a white colour, interspersed with particles of an orange and of a bright blue. From the abraded dust of this sample, obtained by agitation, some of the latter were separated, and proved on examination to be Prussian-blue; the orange portion was apparently some vegetable colour; and the white and principal part was found to contain silica, alumina, a little lime and magnesia, and was probably kaolin or powdered agalmatolite, more particularly from the rubbed and prominent parts of the tea assuming a polished appearance. A great variety of other samples of teas were submitted to examination, but in all cases they were found to be faced with various substances, give them the bloom and colour which is so distinct a characteristic of the green teas of commerce. The unglazed varieties appear to have had no bluing material applied. Very high qualities of glazed teas have this facing apparently tinted of an uniform pale blue before application: while others, still of high quality, and embracing the great part of the samples examined, have both the white and blue particles very distinct, the latter varying in its quantity; in the low qualities, as twankay, being pretty thickly powdered. When this facing was removed, the tea was found to be of a black colour, but without the corrugated aspect presented by black teas ordinarily, and which evidently arises from the higher temperature to which they are subjected during the process of curing or drying. The substances separated from these green teas were sulphate of lime, a material analogous to kaolin, and Prussian-blue, together with some yellow vegetable colouring body. It is evident that the whole of these teas come to this country in a dressed or adulterated state, and the onus of this should fall on the right shoulders.

The author concluded by quoting various opinions and observations of persons long resident in China, by which his investigations are satisfactorily confirmed.

"On the Cyanides of the Metals, and their Combinations with Cyanide of Potassium," by Messrs. Glassford and Napier.

This paper first adverts to the importance of a knowledge of these salts, in reference to the great interest attached to them on account of their extensive practical application in the art of electro-metallurgy; and then proceeds to point out many contradictory and unsatisfactory statements as to the constitution of these salts as hitherto

published in various chemical works. The paper then shows, that the process for the preparation of cyanide of potassium, called "Liebig's process," was first fully detailed in the Philosophical Magazine for February 1834 by Messrs. F. and E. Rodgers, and is that which is in daily operation, viz. by exposure of a mixture of anhydrous carbonate of potash and anhydrous ferrocyanuret of potassium to a moderate heat, in a covered porcelain crucible, for about twenty minutes. The average amount of impurities contained in this salt varies from 35 to 50 per cent.

The paper then proceeds to give a description of cyanide of gold, its mode of preparation, its various properties, and its analyses; and from three experiments closely agreeing with the calculated results, concludes that its composition may be represented by the formula Au + Cy.

Cyanide of Gold and Potassium.—Several modes of preparing this salt are then detailed:—1st, by dissolving cyanide of gold in cyanide of potassium; 2nd, by dissolving oxide of gold (as prepared by means of calcined magnesia) in cyanide of potassium; 3rd, by adding a solution of cyanide of potassium to terchloride of gold; and 4th, by means of the galvanic battery, composed of two or three pairs of zinc and copper plates, excited by dilute acid. From an analysis of this salt, it appears that it consists of—

1 equiv. of cyanide of gold.
1 equiv. of cyanide of potassium.
1 equiv. of water.

Formula, Au Cy + K Cy + HO.

Messrs. Glassford and Napier conclude by stating that the salt described by Müller, as prepared by saturating chloride of gold with cyanide of potassium, is not the aurocyanide of potassium, but the cyanide of gold and potassium, as described in their paper.

"On a new Cyanide of Gold," by Mr. John Carty.

The only cyanide of gold hitherto described contains 3 equiv. of cyanogen to 1 of gold. Indications of the existence of a second compound, containing a smaller proportion of cyanogen, led the author to make certain experiments, which were successful.

Protochloride of gold was decomposed by cyanide of potassium in solution; an abundant pale yellow precipitate appeared, which was redissolved by the alkaline cyanide. To this solution hydrochloric acid in excess was added, and the whole boiled. A yellow powder thrown down was collected, washed and dried by a gentle heat. It was insoluble in water, alcohol and æther; readily soluble in ammonia and in solution of cyanide of potassium. When heated it evolved cyanogen and left metallic gold. It was not decomposed by boiling hydrochloric or nitric acid, or by a solution of chlorine; *aqua regia*, on the contrary, effected its decomposition, slowly in the cold, rapidly at a boiling heat.

30·7 grs. of the substance left of metallic gold after ignition 27 grs.; hence its constituents are very nearly in the proportion of 200 gold to 26 cyanogen, or single equivalents. It must therefore be considered a protocyanide analogous to the protoxide.

Tercyanide of gold, dissolved in hot hydrochloric acid, was gradually reduced to protocyanide on concentration; probably at the expense of a portion of the cyanogen, which was converted into ammoniacal compounds.

A compound of protocyanide of gold and ammonia was also noticed by the author. The double salt with cyanide of potassium may be obtained in long prismatic, milk-white, anhydrous crystals, which are somewhat deliquescent. Mr. Carty considers this substance to contain 1 equiv. protocyanide of gold and 2 equiv. cyanide of potassium.

Mar. 4. (Robert Porrett, Esq., in the Chair.) "On the Cyanides of the Metals, and their Combinations with Cyanide of Potassium," by Messrs. Glassford and Napier.

The best method of preparing cyanide of silver on the large scale is to precipitate a solution of nitrate of silver with cyanide of potassium, to wash the precipitate, and then to digest it in dilute nitric acid, which removes any carbonate or cyanate that may be present. If the cyanide of potassium employed contain chloride or undecomposed ferrocyanide, the silver compound will be contaminated with those compounds. In this case it is better to prepare the double cyanide of silver and potassium, and add to it nitrate of silver. The precipitate which falls is in all cases pure cyanide.

Cyanide of silver is decomposed by hydrochloric acid, by nitric acid when concentrated and boiling hot, and by heated sulphuric acid. It dissolves by the aid of heat in the alkaline chlorides, and in the chlorides of calcium, barium and magnesium. It is also soluble in solution of ferrocyanide of potassium, and forms with that substance one or two crystallizable compounds, which have not yet been examined.

Cyanide of silver combines with cyanide of potassium to a very soluble, crystallizable, double salt, containing single equivalents of its components. The solution yields on evaporation two kinds of crystals, viz. hexagonal plates, resembling chlorate of potash, and small, but very transparent rhombic prisms. The first forms are anhydrous, while the latter contain an equivalent of water. The double salt is easily decomposed by acids, cyanide of silver being thrown down.

A solution of cyanide of potassium decomposes or dissolves all the insoluble compounds of silver with the exception of the sulphuret, the double salt just described being produced. This is also true of the chloride, a chloride of the alkaline metal being generated.

The authors next describe a process, founded on the preceding principles, for determining the per-centage of real cyanide of potassium in any sample of the commercial article, by adding to a weighed quantity dissolved in water, a solution of nitrate of silver of known strength from a graduated vessel, until the precipitate first thrown down ceases to be redissolved on agitation. An equivalent of nitrate of silver thus employed indicates of course 2 equiv. of cyanide of potassium.

It has been observed, that when ferrocyanide of silver is put in

contact with nitric acid, it is immediately converted into ferridcyanide, the white colour changing to deep orange. 2 equiv. of the ferrocyanide yield 1 equiv. ferridcyanide and 1 equiv. nitrate.

When washed ferridcyanide of silver is heated in water to about 150°, it loses its orange colour and becomes green. Any nitric acid or nitrate of silver prevents this change, the nature of which has not yet been examined.

PATENT.

Patent granted to Richard Laming, London, *for certain Improvements in the Purification and Application of Ammonia.*

That part of the invention which relates to improvements in the purification of ammonia, is for the purpose of obtaining ammonia sufficiently pure for many purposes in the arts from gas-liquor, by substituting for the mineral acids usually employed a solution of muriate of lime. The process pursued by the patentee is as follows:—He first mixes with gas-water a sufficient quantity of muriate of lime in solution to convert the carbonate of ammonia which is present into muriate of ammonia; and after having separated the carbonate of lime which forms, the remaining solution is exposed for an hour to a boiling temperature. This solution, after having been cooled, is first agitated with enough hydrated oxide of iron to combine with all its sulphuretted hydrogen; secondly, with lime enough to saturate the muriatic acid which is present; and finally it is distilled. The ammonia will be found in the water, which comes over in a tolerably pure state.

That part of the invention which relates to improvements in the application of ammonia is as follows:—Ferrocyanuret of potassium and ferrocyanuret of sodium, known in commerce as prussiate of potash and prussiate of soda, are usually made by burning animal matter in contact with a carbonated alkali and with iron. The ammonia evolved from the animal matter is partly decomposed by the other substances, and assists in forming with them a heterogeneous mass, consisting principally of potassium or sodium (according to the kind of alkali used), carbonated alkali, cyanogen, iron and charcoal. This mass, by lixiviation and crystallization, affords the ferrocyanuret.

The ferrocyanurets of potassium and sodium are the sources from which, directly or indirectly, the cyanogen used in making all the other ferrocyanurets, cyanurets and hydrocyanates known in commerce, has hitherto been derived.

Commercial prussic or hydrocyanic acid has hitherto been made by decomposing either the ferrocyanuret of potassium, the ferrocyanuret of sodium, or some other ferrocyanuret, cyanuret or hydrocyanate, resulting directly or indirectly from one or the other of

them. It is evident from these facts, that prussic acid can never have been available for the reproduction of any of the cyanurets, ferrocyanurets or hydrocyanates, sufficiently cheap for the purposes of commerce. Now by these improvements ammonia is so applied to the production of cyanogen as to make prussic or hydrocyanic acid the primary result, and at a cost low enough to admit of its application to the œconomical production of the cyanurets, ferrocyanurets and hydrocyanates generally. The improved process is as follows:—A cylindrical retort of cast iron, eight feet long and eighteen inches internal diameter, lined with fire-tiles fitted to its shape, and set vertically in a furnace, is filled with pieces of charcoal, and brought to a red heat. Ammonia, more or less pure, in the form of gas, or even combined in a state of vapour with certain other substances which do not prevent the desired result, is introduced by a pipe near one end of the heated retort. In its passage the ammonia is deprived of its constituent hydrogen; while the remaining part, together with its nitrogen, combine with carbon to form prussic or hydrocyanic acid, which finally escapes from the heated vessel in the form of vapour, accompanied by other elastic matters, amongst which will be, if the admission of ammonia into the retort has been too rapid, some of that substance in an undecomposed state. The prussic acid vapour thus obtained may be condensed in water, or by other convenient means, for subsequently making the compounds of cyanogen, or other purposes; or it may be brought at once into communication with the several substances with which it or its constituent cyanogen is to be combined. Thus, for example, it may be received into caustic solutions of the fixed alkalies, and with them made to dissolve iron, giving rise, in the first instance, to solutions of hydrocyanates of potash and of soda, and afterwards to solutions of the ferrocyanurets of potassium and of sodium; or it may be received into water containing certain metallic oxides, with which it will make the corresponding metallic cyanurets or hydrocyanates. The means for producing chemical products by the saturation of acids with different bases, are too well known to chemists to render necessary any further detail of the means to be adopted for obtaining hydrocyanates, cyanurets or ferrocyanurets, by the chemical combination of hydrocyanic acid and the several bases.—Sealed July 13, 1843.

THE CHEMICAL GAZETTE.

No. XXXVII.—May 1, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Bilic Acid. By MM. THEYER and SCHLOSSER.

THE facts contained in this article are further confirmations of the circumstance pointed out by Liebig, viz. that biliary matter, freed from mucus, fat and colouring matter, is really nothing more than bilate of soda; and that Thenard's picromel, Kemp's bilic acid, Demarçay's choleic acid, Berzelius's bilifellinic acid, and the organic substance contained in addition to soda in biline, are in reality the same organic acid, but which, on account of their ready decomposition, are difficult to obtain pure. It is on account of this difficulty of purifying the hitherto obtained product, that the properties of the above-mentioned body, as given by those who have prepared it, often differ in some points from the properties of pure bilic acid.

Pure Bile.—Perfectly fresh ox-gall, strained through linen and inspissated by evaporation, is treated with ordinary alcohol in the cold, and this added until no more precipitation takes place. The biliary mucus is now separated by filtration, and the liquid digested at the ordinary temperature with bone-black for twelve hours, being frequently shaken, then filtered, the alcohol distilled off from the colourless liquid, the syrupy residue repeatedly agitated with æther until this removes nothing more, and finally dried in a water-bath. The pulverized residue resembles gum-arabic, is colourless and distinctly alkaline, soluble in water and alcohol, but not in æther. When incinerated it yields an ash abounding in common salt and carbonate of soda. It tastes bitter, subsequently sweetish, and the powder causes coughing and sneezing. The aqueous solution is unaltered by acetic or oxalic acid; muriatic acid precipitates a resinous mass, and the liquid then contains soda; nitrate of silver produces a white plastery precipitate, which soon becomes brown; perchloride of iron a brownish-red and greasy, and perchloride of tin a white precipitate. Neutral acetate of lead gives a white precipitate, and in the filtered liquor basic acetate of lead throws down another precipitate. If the solution is previously treated with acetic acid, neutral acetate of lead causes no precipitate; basic acetate of lead produces a precipitate when a small quantity only of acetic acid is present. The precipitates with lead are soluble in alcohol. Barytic water, barytic salts, lime water and perchloride of mercury produce no precipitates. In the

alcoholic solution of the bile, oxalic acid produces a crystalline precipitate of oxalate of soda; neutral acetate of lead gives no precipitate, and diacetate only a slight one; the latter is dissolved when neutral acetate is added. Lime and barytic water render the solution turbid; this turbidity disappears when water is added; perchloride of iron and bichloride of mercury produce no alteration; protochloride of tin a precipitate disappearing by heat. Pure bile, dried at 212°, consists of—

Carbon	58·00	58·49	59·48
Hydrogen	8·09	8·48	8·47
Nitrogen	3·62		
Oxygen	20·65		
NaO	6·08		
NaCl	3·56		

Bilate of Lead.—If a solution of pure bile in a considerable quantity of water is mixed with diluted solution of diacetate of lead, so that the liquid always remains alkaline, warmed and shaken, a tenacious plastery precipitate is obtained; the supernatant liquid is poured off, the mass washed with water until this removes no more soda or lead; it is then dissolved in warm alcohol, the undissolved chloride of lead separated by filtration, and the filtered liquid evaporated in a warm bath. A white pulverulent residue is obtained, which is soluble in alcohol, insoluble in cold water, becomes adhesive by boiling in water, frothing like soap. From the alcoholic solution of this salt of lead all the lead is separated by sulphuric acid, and the solution of the organic matter soon becomes troubled, and exhibits numerous alterations of colour when excess of acid is present. The lead salt, dried at 212°, consists of—

Carbon	40·78	40·81	41·04
Hydrogen	5·92	5·98	5·81
Nitrogen	2·29		
Oxygen	13·95		
PbO	37·06	36·93	

If, in preparing the lead salt, the diacetate of lead is added to a solution of bile mixed with ammonia, a plastery precipitate likewise falls, which, when treated with water and dissolved in alcohol, is separated from a basic acetate and chloride of lead, and, when dried at 212°, consists of—

Carbon	36·69	36·86	37·03
Hydrogen	5·16	5·38	5·24
Nitrogen	2·11		
Oxygen	12·85		
PbO	43·19	43·09	

Bilate of Soda.—The salt of lead first spoken of is rendered saponaceous by boiling water; crystallized carbonate of soda is then added to the warm liquid, which is constantly shaken, until all the lead is separated in the form of carbonate. The filtered liquor is evaporated to dryness, the residue dissolved in anhydrous alcohol;

the excess of carbonate of soda is thus left, and the filtered liquor evaporated in a water-bath. The residue perfectly resembles in colour, odour, taste and behaviour to reagents the pure biliary matter, the only difference being that muriatic acid more readily produces a precipitate, and that acetic acid in excess, when the liquid is warm, produces a precipitate soluble in alcohol. The bilate of soda is only distinguished by the absence of the chloride of sodium, and a somewhat less intimate union of the ingredients of the bile. The composition of both is exactly the same when the analysis of the pure bile is estimated, after deducting the amount of chloride of sodium :—

	Bile.		Bilate of soda.	
Carbon	60·14	60·12	59·60	59·16
Hydrogen	8·38	8·62	8·60	8·55
Nitrogen	3·75	3·32	3·30	
Oxygen.....	21·43	20·99	21·82	
NaO	6·30	6·95	6·68	6·41

Bilic Acid.—Dried and powdered bile was dissolved in anhydrous alcohol at a gentle heat, and dry oxalic acid added to it, and heated in a water-bath until it began to boil slightly. On cooling, a crystalline sediment was formed, which was composed of common salt, oxalate of soda and free oxalic acid. The liquid however left on incineration a residue ; it was consequently again treated with oxalic acid as before. A further precipitation now occurred ; the liquid had dissolved some oxalic acid, but contained no soda. The filtered liquid was treated with freshly precipitated, well-washed carbonate of lead, to free it from the oxalic acid in solution ; effervescence from the escape of carbonic acid was now perceptible, and the solution freed from soda showed barely traces of lead. A stream of sulphuretted hydrogen was now passed through it, the whole slightly warmed, and allowed to repose for some time ; when filtered, a bright yellow transparent liquid was obtained, of a pungent and bitter taste, which left, on evaporation in a water-bath, a brown, tenacious, resinous cake, which when cold was reducible to powder with tolerable ease, and formed a bright yellow powder. It dissolved in water, but rendered it milky, and the solution could not be separated by filtration from the white substance suspended in it. When dried and treated with æther, some of it was dissolved, forming, when the æther was evaporated, a white mass, insoluble in water but soluble in alcohol. Another portion of the dried substance was dissolved in a little water, and treated with a considerable quantity of æther until no more was taken up ; the æther was then poured off, and the liquid evaporated in a water-bath. If it was now dissolved in anhydrous alcohol, a residue remained, which was insoluble in æther, soluble in water, and crystallized from it in transparent, shining needles, and by elementary analysis was proved to be taurine. If the alcoholic solution was now evaporated in a water-bath and dissolved in water, a milkiness again ensued : by repetition of the same operation, we have always the same two products of decomposition to deal with, and we only succeed with very small quantities in obtaining at last

a mass perfectly soluble in water and alcohol, insoluble in æther, which is not altered by acetic acid, and forms a white precipitate with muriatic acid, which, when the muriatic acid is separated, is again soluble in water.

Another method of isolating the acid was the following:—A portion of purified bile was dissolved in a little water, treated with muriatic acid not too concentrated, shaken, and then allowed to repose. An oily liquid formed on the bottom of the vessel, which for several days increased. If it be allowed to remain until no more separates, the greater part of the soda of the bile is found in the supernatant liquid; on evaporation, chloride of sodium crystallizes and oily drops form, which, when taken out, on cooling become hard, and possess similar properties to those of the oily liquid, viz. when dissolved in water, are precipitated by muriatic but not by acetic acid. However, by this process the substance is not entirely freed from soda and muriatic acid. Bilic acid was finally obtained pure by the following method:—The purified bile was dissolved in a small quantity of water, and precipitated without heat by diacetate of lead, the plastery precipitate immediately washed, dissolved in weak warmed alcohol and filtered; sulphuretted hydrogen was then passed through the filtered liquid, which was not treated with sulphuric acid, until all the lead was precipitated; it now became clotted, which is easily prevented by the addition of more alcohol; the whole was now gently warmed for half an hour and filtered, whereby the sulphuret of lead was perfectly removed.

The application of a gentle heat is necessary to prevent the sulphuret of lead from passing through the filter. The liquid, which is now perfectly free from soda and chloride of sodium, is allowed to repose for some time, whereupon a little sulphur separates, and is again filtered; this must be repeated several times during evaporation to ensure accuracy. The whole operation is concluded in half a day, and, through the simplicity of the operations, all decomposition avoided. During evaporation the temperature must not exceed 140° Fahr. It is best to evaporate the whole of the liquid to dryness *in vacuo* over sulphuric acid. If it is evaporated in a water-bath, *i. e.* in boiling water, decomposition always ensues; the substance no longer forms a clear solution in water, but renders it milky.

The acid obtained by this process, when dried and pulverized, forms a white powder, having very much the appearance of powdered sandarach, and is very hygroscopic; when kept for some time at the temperature of boiling water, it becomes brown; at a somewhat higher temperature it melts, puffs up and burns with a strong odour. The cinder leaves no ash. It is insoluble in æther, but dissolves completely and readily in alcohol, as also in water, and forms a colourless clear solution, of a bitter astringent taste, strong acid reaction, which is not altered by acetic or oxalic acids; muriatic acid causes a white resinous precipitate, which on pouring off the acid and washing with water again dissolves. Boiled with nitric acid, a resinous mass separates. Lime water causes no precipitate. When

the mass is boiled with barytic water, it is completely precipitated, a peculiar odour of glue being developed and the acid decomposed. When digested for some time with carbonated alkalies, carbonic acid is separated, whilst the alkali combines with the acid. With nitrate of silver a yellow precipitate is formed, which becomes brown by exposure to air. Neutral and diacetate of lead produce precipitates which are soluble in alcohol. An aqueous solution of the acid, when copiously diluted, remains several days without any perceptible change. When exposed to the air for some time in the form of powder, it becomes decomposed, and is no longer completely soluble in water. An alcoholic solution, preserved for some time, forms a white sediment, which, when dissolved in water and evaporated, separates in crystalline needles, and is taurine.

When analysed it yielded as follows :—

Carbon	63·70	63·76	63·98
Hydrogen	8·84	8·50	8·58
Nitrogen	3·97	3·45	
Oxygen	23·49	24·29	

If, omitting the soda, the above analyses of the bile (No. 2), bilate of soda (No. 1), and the mean of the analyses of the lead salts be compared, we obtain the same result, save a difference presently to be mentioned, whereby the identity of the isolated bilic acid with that in the compounds we have spoken of is proved :—

	Bile.	Bilate of soda.	1st salt of lead.	2nd salt of lead.
Carbon	64·730	64·610	64·901	64·807
Hydrogen	9·384	9·264	9·373	9·247
Nitrogen	4·006	3·568	3·638	3·714
Oxygen	21·880	22·558	21·088	22·232

In the latter analyses there appears more carbon and oxygen than in the analyses of the bilic acid. The free bilic acid is thus probably a hydrate. If we subtract an amount of water corresponding to that of the soda of the bile (2·065 per cent.), the identity is almost complete. If the bile is a neutral compound, the atomic weight of bilic acid is = 5600. The authors have however avoided the construction of a formula, until some of its products of decomposition have been more minutely examined, because the estimation of the equivalents of hydrogen is difficult on account of the high atomic weight.—*Ann. der Chem. und Pharm.*, xlviii. pp. 77–95.

On Hippuric and Acetic Acids in the Urine of Man. *By* Prof. Liebig.

When fresh urine is evaporated over the water-bath to the consistence of a thin syrup, and on cooling one-twentieth part of strong hydrochloric acid added to it, then shaken with æther, this dissolves the hippuric acid which has separated. It frequently happens that the æther, as in an emulsion, separates with difficulty from the resin; but this is instantly effected by the addition of a few drops of alcohol. In this case the æthereal solution of the hippuric acid should be

shaken previous to evaporation with some water, in order to remove the urea taken up by the æthereal solution through the intermediation of the alcohol. When this is done, crystals of pure hippuric acid are obtained on evaporation of the æthereal solution. It was not absent in any of the numerous human urines examined during the last six months. Stale urine no longer contains any hippuric acid, but in its stead benzoic acid, as was long ago observed by Proust. When putrid urine is evaporated without any addition of potash to retain the benzoic acid, a large portion of it isvolatilized along with the ammoniacal vapours.

When concentrated putrid urine is submitted to distillation with a mineral acid, a considerable quantity of acetic acid, accompanied by benzoic acid, is obtained. This had likewise been observed by Proust. I have prepared with this acetic acid several ounces of the lead salt and of other salts, which, as well as the hippuric and benzoic acids, have been submitted to analysis; so that there can be no doubt respecting the nature of these products and educts. By product I mean the acetic acid, for I have never been able to find it in fresh urine, nor could I detect any lactic acid. It is much to be regretted, that after Berzelius's great discovery of the peculiarity of lactic acid and of its distinctness from acetic acid, in all the statements in the subsequent editions of his classic Manual, when the observers had found acetic acid, this acetic acid has been changed into lactic acid. From this time dates the wide distribution of this acid in the animal body, for none of the subsequent investigators of such bodies have taken the trouble to make any further examination.—*Archiv der Pharm.* for March.

Observations on Oil of Chamomile.

The essential oil of *Matricaria Chamomilla,* characterized by its deep blue colour, has not hitherto been submitted to closer examination. It is not known whether the colour is peculiar to it or to some volatile body dissolved in it, or whether it consists of one or several oils, of which perhaps one is blue, the other colourless. The small quantity which is obtained of this oil and its high price have hitherto prevented its being more closely examined. Some experiments undertaken by M. Bornträger, with an oil obtained from pure chamomile flowers, gave the following results:—

On rectification with water it retains its deep blue colour; the first drops are quite as blue as the last. The water which distils over with it is colourless. If this be shaken with æther, it leaves on evaporation a very small quantity of a nearly colourless oil, the odour of which is essentially different from that of the blue oil.

The blue oil dissolves in alcohol and in æther with a blue colour; when cooled below 32°, it becomes so thick as to appear nearly solid; however, no stearoptene could be separated from it in this manner, although there are frequently found distinct laminæ of a colourless stearoptene in the commercial oil when very thick.

Four analyses of the oil, which had been in contact for fourteen

days with fused chloride of calcium, afforded the following numbers:—

	I.	II.	III.	IV.
Carbon.....	79·85	79·81	79·61	78·26
Hydrogen....	10·60	10·69	10·83	
Oxygen.....	9·55	9·50	9·61	

The analyses III. and IV. were made with an oil which had been distilled alone, No. III. was what passed over first, No. IV. was made with the last portion. A brown resinous mass remained in the retort. The gas of the oil is perfectly colourless.—Liebig's *Annalen* for Feb. 1844.

On the Occurrence of Mannite in Agaricus piperatus.

It has long since been proved that the sweet substance contained in several fungi, for instance in *Cantharellus esculens* and *Clavellaria coralloides*, was nothing but mannite, which rendered it probable that Braconnot's so-called mushroom-sugar, said to be fermentable, was only a mixture of mannite with one of the known kinds of sugar. But it was also probable that certain other fungi might indeed contain a peculiar fermentable sugar. This induced MM. Knopp and Schnedermann, in their investigation of the acrid substance contained in *Agaricus piperatus*, likewise to direct their attention to the mushroom-sugar. It was proved, both from the properties and by analysis, that the sweet substance contained in this fungus is likewise mannite, which could be separated from it in considerable quantity. A large amount of these fungi were pressed, the sap treated with sugar of lead and then with sulphuretted hydrogen, evaporated to an extract, this exhausted with alcohol, and the alcohol distilled from the solution. The residue solidified to a brown crystalline mass, from which colourless mannite was readily obtained by repeated treatment with alcohol and animal charcoal.—Liebig's *Annalen* for Feb. 1844.

On Assamar. By M. Von Reichenbach.

The substance to which the author has applied this name is the cause of the bitter taste developed in organic bodies by roasting and baking them; it occurs therefore in the dark brown crusts of bread, roast meat, in the brown malted corn, and is consequently daily consumed by man. Assamar is found in great abundance in roasted coffee, and in all the roasted substitutes for coffee without exception; it is constantly formed in the preparation of decoctions and extracts when the liquids burn at the bottom of the vessel, in baking, boiling, &c. under the most varied conditions. The becoming moist and softening of originally dry-baked crusts of bread, &c., is owing to the hygroscopic property of the assamar, which is even capable of depriving alcohol of water; it is also on this account that caramel so readily becomes moist.

It is extremely difficult to obtain assamar in a pure state, since

this body does not crystallize, cannot be distilled, is perfectly neutral, and at the same time is hygroscopic and readily decomposed; it moreover is always accompanied with perceptible traces of lime, derived from the bodies from which it originates, and of which it is extremely difficult to deprive it. Assamar may be extracted from almost all animal and vegetable substances which have been roasted on a tin plate, exposed to the air, to a blackish-brown colour, by repeated treatment of the cold pulverized mass with ice-cold absolute alcohol in closed vessels. The author generally employed pulverized roasted wheaten bread, to which no salt had been added. It is known to be sufficiently roasted when it possesses the most intense bitterness. Nitrogenous bodies and sugar afford most assamar, starch and gum less, woody fibre none.

The preparation therefore commences either with the repeated extraction of the substance with cold absolute alcohol, or it is first exhausted with water, evaporated, the extract exhausted with alcohol, again evaporated, and this extract now treated with absolute alcohol; or lastly, weak alcohol is employed first, and the obtained extract exhausted. The latter methods require, it is true, much alcohol and more time, but they require less absolute alcohol, and afford a larger amount of product. Bodies roasted in a pulverulent state give less assamar than when roasted in compact masses. The alcoholic solution is of a wine-yellow colour, and contains less foreign ingredients the more anhydrous and the colder the alcohol employed; it is distilled to a syrupy consistence*. The residue, an alcoholate of the assamar, is treated with a little water, and the remainder of the alcohol distilled off, upon which the aqueous syrup is allowed to cool. Some fat separates, which is removed with æther. The faintly acid syrup is now cautiously neutralized with lime milk, and nearly heated to boiling, when a brown flocculent precipitate is formed. Small quantities of absolute alcohol are added to it, warming each time until the milky precipitate has disappeared; when this is no longer effected, no further addition of alcohol is made, but the whole is placed aside to cool, when the liquid again deposits a sediment. The liquid is poured off, and the residue remaining in the retort, which is of a white colour and easily removed by water, washed with alcohol. The liquids are now again distilled, and the syrup treated with alcohol as above, which is continued until the solution on cooling affords no further deposit. Anhydrous æther is now added, which produces an opacity and a tenacious precipitate; if this be sweet and insoluble in cold absolute alcohol, it is set aside and more æther added until a purely *bitter* precipitate is formed. The mixture is now submitted to distillation, when the residue obtained is an aqueous solution of assamar, which may be dried in small quantities by cautious heating; but too high a temperature and access of air should be very carefully avoided, otherwise decomposition ensues. It was found impossible to deco-

* When it has been prepared from sugar, there separates, on allowing it to cool, some unaltered sugar, the solubility of which in absolute alcohol was effected by means of the assamar.

lorize assamar by means of charcoal; the liquids become colourless, but at the same time lose their bitterness, because the assamar is absorbed by the charcoal. Pure assamar is probably of an amber-yellow colour; it appears of a gamboge-yellow in milky precipitates.

Assamar is gummy, compact, yellowish, very brittle, has a conchoidal fracture, with vitreous lustre, a pure bitter agreeable taste, and a very faint, somewhat aromatic odour. It melts on being heated, and solidifies on cooling to a mass full of fissures; it is not volatilized by heat, but is entirely decomposed, with evolution of combustible vapours, leaving behind a carbonaceous residue. It rapidly absorbs moisture from the atmosphere, and deliquesces in hydrated alcohol, depriving it of water. It dissolves in every proportion in water; on heating the solution with access of air the colour gradually becomes darker, the bitter taste decreases, and in place of the assamar we now find only the substance above described, which is precipitated by alcohol; it is therefore only possible to obtain assamar undecomposed by the evaporation of aqueous solutions, by taking very minute quantities and employing the greatest care. Alcohol of 0·83 spec. grav. dissolves assamar slightly in the cold and abundantly when warm. Absolute alcohol dissolves most at a boiling heat; it is insoluble in æther, which the more completely precipitates the assamar from an alcoholic solution the more anhydrous the solution and the æther.

The solutions of assamar are neutral; they are also on boiling perfectly indifferent towards oxide of mercury, oxide of copper and hyperoxide of lead; they are decolorized by nitric acid, without any formation of oxalic or mucic acids. Concentrated sulphuric acid renders them black; chromate of potash is without effect; nitrate of silver is reduced; chloride of gold affords a bluish-black, acetate of copper at a boiling heat an orange-yellow precipitate; chloride of platinum, sulphate of copper, peracetate of iron, cause no alteration, nor do the neutral and basic acetates of lead in a solution of pure assamar; but if the solutions are impure, brown precipitates are formed. Without action are moreover muriate of tin, muriatic acid, ammonia, potash, lime water and barytic water; impure solutions are rendered of a darker colour by alkalies, and are precipitated brown by lime; the alkalies however are not neutralized, but on heating the alkaline solutions the bitter taste disappears and the assamar is decomposed. Borax, tincture of galls, isinglass, yeast and silicate of soda have no effect.—*Ann. der Chem. und Pharm.*, xlix. p. 1–17.

On the Products resulting from the dry Distillation of the Sulphocyanurets. *By* M. C. Gerhardt.

I have recently had the opportunity of studying the very interesting bodies which M. Liebig obtained in the dry distillation of the sulphocyanurets. This investigation has led to the discovery of several errors, which occur in all chemical treatises, and which cause great confusion in the history of these bodies. It will how-

ever be seen that there is great simplicity in their numerous metamorphoses.

When sulphocyanuret of mercury is distilled, sulphuret of carbon and cinnabar are produced, as well as the orange-coloured body to which M. Liebig has given the name of *mellon*. This latter contains $C^3 N^4$ *. M. Völckel has recently disputed the accuracy of this formula; but it is impossible to substitute any other for it. It will also be seen that the formation of mellon from other compounds entirely agrees with M. Liebig's formula. Mellon is thus derived from the sulpho-cyanuret of mercury:—

$$4CHgNS = CS^2 + 2Hg^2S + C^3N^4 \dagger.$$

When M. Wöhler's persulpho-hydrocyanic acid, $C^2 H^2 N^2 S^3$, is heated in an oil-bath, it is entirely decomposed, and produces sulphuret of carbon, sulphuretted hydrogen, and a residue, from which a higher temperature expels some sulphur, leaving a grayish body, which still contains some mellon:—

$$2C^2 H^2 N^2 S^2 = CS^2 + 2H^2 S + C^3 N^4 + S^2.$$

This mellon does not constitute a radical. It dissolves in caustic potash without disengagement of hydrogen, and acetic acid precipitates white flakes of M. L. Gmelin's *hydro-mellonic acid* from the solution. But this acid contains oxygen as an integral part. The mellonuret of lead, obtained by mixing the salt of potash with some nitrate of lead, contains $C^3 (HPb) N^4O + 2Aq$, as the analyses of M. Gmelin prove. The 14·5 per cent. of water of crystallization, which this salt contains, are expelled by drying, but the dry salt contains oxygen. It is moreover impossible that it should be otherwise, for mellon directly fixes the elements of the potash (KH) O, as does, for example, isatine on its conversion into isatate, or camphor when being converted into Delalande's campholate. We have therefore—

Hydromellonic acid	$C^3 H^2 N^4 O$.
Mellonuret of potassium	$C^3 (HK) N^4 O$.
Mellonuret of lead	$C^3 (HPb) N^4 O$.

That hydromellonic acid does not possess the composition which the theory of radicals attributes to it, is moreover proved by this body giving, on being heated in a glass tube, some mellon and water, as well as hydrocyanate of ammonia, arising from a secondary action of the water on the elements of the mellon. We have therefore—

$$C^3 H^2 N^4 O = C^3 N^4 + H^2 O.$$

From the above it is also seen, that the entirely pure and dry mellon could not give a mellonuret by the action of the potassium; for whence would then come the hydrogen that the mellonuret of potassium contains?

* We have preferred leaving the author's notation unaltered in the present instance. The general method of writing mellon is $C^6 N^4$, and water HO.—Ed. *Chem. Gaz.*

† C = 75, H = 6·25, N = 87·5. The oxides corresponding to water, $H^2 O$, are represented by $Pb^2 O$, $Hg^2 O$, $Ag^2 O$, &c.

A boiling solution of potash attacks the mellon with disengagement of ammonia, and converts it into a salt, from which acids precipitate cyanuric acid. This decomposition also results from the fixation of the elements of the potassium or of the water; for

$$C^3 N^4 + 3H^2 O = NH^3 + C^3 H^3 N^3 O^3,$$
$$C^3 N^4 + 3(KH) O = NH^3 + C^3 K^3 N^3 O^3.$$

Let us pass to the dry distillation of the sulpho-hydrocyanate of ammonia. This salt gives some sulphuret of carbon, sulphuretted hydrogen, ammonia, and a grayish residue, to which M. Liebig has assigned the name of melam. This body, in my opinion, is only a mixture of mellon and of the alkaloid called melamine; it possesses all the characters peculiar to a similar mixture. As melamine contains $C^3 H^6 N^6$, we have—

$$4CHNS, NH^3 = CS^2 + 2H^2 S + 2NH^3 + C^3 H^6 N^6.$$

The presence of mellon may be explained, if we consider that the melamine itself is converted at a high temperature into mellon and ammonia:—

$$C^3 H^6 N^6 = 2NH^3 + C^3 N^4.$$

Under the influence of alkalies, or of concentrated acids, melamine fixes the elements of water, eliminates ammonia, and is successively transformed into *ammeline, ammelide* and *cyanuric acid*:—

$C^3 H^6 N^6 + H^2 O = NH^3 + C^3 H^5 N^3 O$ ammeline.
$C^3 H^6 N^6 + 2H^2 O = 2NH^3 + C^3 H^4 N^4 O^2$ ammelide.
$C^3 H^6 N^6 + 3H^2 O = 3NH^3 + C^3 H^3 N^3 O^3$ cyanuric acid.

Ammeline and ammelide are at last converted into cyanuric acid. By the action of heat ammeline and ammelide also afford mellon. We have indeed—

$$C^3 H^5 N^5 O = NH^3 + H^2 O + C^3 N^4.$$
$$C^3 H^4 N^4 O^2 = 2H^2 O + C^3 N^4.$$

Nothing is more simple than these metamorphoses; the question is always the fixation or elimination of the elements of water or of ammonia, as in the greater part of organic reactions. But what renders M. Liebig's three alkaloids still more intertesting is, that they represent the *amides* corresponding to the three ammoniacal salts of cyanuric acid. This latter, as a tribasic acid, ought to combine with ammonia in giving—

$C^3 H^3 N^3 O^3$ NH^3 monobasic salt,
$C^3 H^3 N^3 O^3$ $2NH^3$ bibasic salt,
$C^3 H^3 N^3 O^3$ $3NH^3$ tribasic salt,

in the same way that oxalic acid, which is bibasic, gives ammoniacal oxalate (which is called an acid salt) and binammoniacal oxalate (or neutral salt). Now it is known that these two oxalates are converted into amides on elimination of the elements of the water:—

$C^2 H^2 O^4$, NH^3, $H^2 O$ = Balard's oxamic acid.
$C^2 H^2 O^4$, $2NH^3$, $2H^2 O$ = Dumas's oxamide.

Apply these equations to the three cyanurates, and we have—

$C^3 H^3 N^3 O^3$, NH^3, $H^2O = C^3 H^4 N^4 O^2$ ammelide,
$C^3 H^3 N^3 O^3$, $2NH^3$, $2H^2O = C^3 H^5 N^5 O$ ammeline,
$C^3 H^3 N^3 O^3$, $3NH^3$, $3H^2O = C^3 H^6 N^6$ melamine.

The transformation of these three alkaloids into ammonia and cyanuric acid, under the influence of the concentrated alkalies and acids, proves, I think, the correctness of my opinion. It is true that, to adopt it, we must give up the hypothesis of amidogen, in order to explain the reactions, by establishing equations such as the above. I have moreover pursued a similar course in my work, and everything leads me to believe that it would be an advantageous substitute for the vague and confused system which is based on hypothetical radicals.—*Comptes Rendus*, Jan. 22, 1843.

Alteration of Colour of the Sulphate of Oxide of Chrome.

M. Krüger precipitated a solution of crystallized chrome alum with alcohol; the salt was deposited unaltered, and dissolved entirely and immediately in water of a violet colour; but when a quantity of the violet solution was heated till it had become green, and alcohol then added to it, sulphate of the oxide of chromium subsided as an oily liquid, which subsequently became solid on depriving it of water. The alcoholic liquid contained no chromium, but a quantity of sulphuric acid, amounting to from 4·6 to 4·4 per cent. of the employed chrome alum, therefore about half the entire amount of the sulphuric acid of the salt: the action of heat is therefore to separate the sulphuric acid. If the green solution is allowed to stand, sulphuric acid is again gradually taken up, and the colour becomes violet; but when the separated sulphuric acid has been removed by alcohol, the solution remains green and gives no crystalline double salt. When the sulphate of the oxide of chrome is heated until it has become rose-red, a basic sulphate of chrome is obtained, which is perfectly insoluble in water, and contains only half the sulphuric acid.—Poggendorff's *Annalen*, lxi. p. 218.

On Paracyanogen and Paracyanide of Silver.
By Harald Thaulow.

The author observed, that when cyanide of silver is exposed in a retort to a slowly-progressive heat, it acquires a darker colour, melts, becomes black, begins to boil, and then exhibits a peculiar phænomenon of ignition, exactly similar to that which happens under the same circumstances with Prussian blue, ferrocyanide of ammonium and ferrocyanide of lead. This phænomenon is accompanied by a violent disengagement of gas, which carries with it a brownish powder from the mass itself, but which is deposited in the tube if this be sufficiently long, before the gas makes its exit, and the latter then becomes colourless. A light gray porous body is left in the retort, which had been previously observed by Liebig and Redtenbacher, who considered it to be carburet of silver;

it is however paracyanide of silver, and it would seem as if the luminous phænomenon was produced by the transition of the cyanogen into paracyanogen. The gas, according to the experiments of M. Thaulow, possesses precisely the same composition and the same specific gravity as cyanogen gas; but its odour is different, and is very characteristic, from the violent irritation which it produces on the mucous membranes of the nose and windpipe; and on respiring air containing but a very small admixture of it, illness and vomiting result. It condenses at 28° F., without any greater pressure, to a colourless liquid, which resumes its gaseous form on the temperature being raised. Water dissolves 4 times its volume of the gas at 59°, but the solution soon decomposes, when it reddens blue litmus-paper and deposits paracyanogen; on the other hand, a solution which contains only 1 volume of the gas, may be preserved for a long time without undergoing any change. It produces a whitish-gray precipitate in a neutral solution of nitrate of silver. The gas is absorbed by a solution of potash; if the solution is dilute it acquires a yellow colour, but if concentrated it becomes brown and deposits paracyanogen. On saturating as accurately as possible the yellow solution in dilute potash by weak nitric acid, no Prussian blue is formed on the addition of a protosalt of iron. If the solution of the iron-salt is concentrated, and the free alkali has not been entirely saturated, a dirty green precipitate is obtained, which acquires a bluish tint by exposure to the air, but which has no resemblance to Prussian blue. The precipitates which salts of lead and of silver form in the yellow neutralized potash solution are white, and far more soluble in nitric acid than cyanide of silver. From these properties M. Thaulow concludes that this gas is a third isomeric modification of cyanogen; and we are actually acquainted with three chlorides of cyanogen which have the same composition, but differ considerably from one another by their properties, so that it is very possible that their difference has its origin in the dissimilar isomeric modification of the cyanogen contained in each of the compounds.

Thaulow heated Prussian blue in a retort, and collected the gaseous products in a recipient; the gas which did not condense was wholly absorbed by potash. Small crystals of an ammonium salt form in the recipient and in the neck of the retort, which produce the same reactions with metallic salts as potash saturated with the gas from cyanide of silver. Moreover, a brown solution of this salt in water occurred in the recipient. This ammonium salt gave off an odour of ammonia, but did not resemble the cyanide of ammonium in its crystalline form, and a much higher temperature was required to volatilize it.

Paracyanogen is obtained when the paracyanide of silver is treated with dilute nitric acid, in which the silver dissolves, leaving behind a blackish-brown powder which still contains silver, and from which it is not possible to extract in this manner the whole of the silver without destroying at the same time the paracyanogen. The residue is well washed, dried, and a quantity of concentrated sulphuric acid

poured over it, forming a dark brown liquid, which deposits pure paracyanogen when dropped into water, while the silver remains in solution. When dry it forms a brown powder, which is insoluble in water and in alcohol, but dissolves in the cold in concentrated sulphuric acid, nitric acid and hydrochloric acid, and likewise in the caustic and carbonate alkalies. The solutions are of a brown colour.

M. Thaulow states, that the residue of Prussian blue and ferrocyanide of lead, when they have been heated until the above-mentioned luminous phænomenon has taken place, affords, by treatment, first with nitric acid, and subsequently with concentrated sulphuric acid, a brownish liquid, from which paracyanogen is precipitated by water.

Berzelius has repeated these experiments on the ferrocyanide of lead and ferrocyanide of potassium, and treated the ignited residues according to the method above described; but on filtering the acid through a funnel containing asbestos, scarcely a trace of paracyanogen was precipitated from it by water. Some carbon remained in the funnel, which after washing did not afford a trace of ammonia on heating with hydrate of potash and lime. It is therefore most eligible to employ the cyanide of silver for the preparation of paracyanogen; in this manner it never fails, and the silver is always re-obtained.

Paracyanide of silver is an ash-gray porous body, which assumes under the polishing steel a metallic lustre analogous to that of bismuth. It may be reduced to the finest powder, which has almost a black colour. It is not altered by exposure to the most intense heat in a crucible lined with charcoal; when heated in the open air, it is only decomposed at the surface, which becomes silver-coloured from the reduced silver, but it remains unaltered in the interior. Surrounded by magnesia and exposed to the above high temperature, it is converted into metallic granules, which no longer contain any paracyanide of silver, but constitute a metallic alloy of silver with magnesium. Paracyanide of silver may be fused with mercury to a gray crystalline amalgam of remarkable hardness. The composition of this paracyanide of silver is represented by the formula, 2 equiv. of silver and 1 equiv. paracyanogen.—Berzelius's *Jahresbericht,* xxiii. p. 81.

ANALYTICAL CHEMISTRY.

On a new Method of determining Sulphur quantitatively in Mineral Sulphurets.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,

In the course of some experiments on a simple method of determining the sulphur and phosphorus in the proteine, and other analogous organic compounds (which I hope shortly to be able to lay before the chemical public in detail), it was obvious that the same

plan may be adopted with advantage in determining the quantity of sulphur in mineral sulphurets. The application of this method to the analysis of copper ores in the moist way is particularly convenient, as the silica, iron, copper and sulphur may thus be determined with great œconomy of time and labour.

You may remember that I was engaged at Giessen, during the year 1842, in determining the sulphur in albumen, fibrine, &c., by passing a current of oxygen over those bodies at a high temperature, receiving the SO^2 formed into Will's apparatus, containing strong nitric acid, in order that the SO^2 might be converted into (SO^2+O). A short account of this method was published in Buchner's 'Repertorium,' but I have subsequently found that the operation is performed with more certainty and convenience by presenting the oxygen to the bodies in a nascent state, and thus converting the sulphur into SO^3 in one operation.

The object however at present is merely to show the application of this mode to the analysis of copper ores, as conducted under my direction by my pupil Mr. Peake.

A portion of the ore was carefully mixed with about three times its weight of pure chlorate of potash, previously fused, and the mixture introduced into a Bohemian glass tube about six inches in length; another portion of chlorate was used to remove the last portion of the mixture from the mortar, finishing the contents of the tube by adding another small quantity of perfectly pure chlorate in powder. The tube was thus nearly one-third filled. Having provided a passage for the gas given off in the usual way, the tube was now exposed to the heat of a Berzelius's spirit-lamp, commencing at the upper part of the mixture and proceeding downwards; in the course of a few seconds the oxidation was complete, and the contents of the tube, when cold, carefully washed out with nitro-hydrochloric acid into a small digesting flask, and placed on the sand-bath; after a few minutes' digestion was obtained a clear solution, containing all the copper, iron and sulphate of potash, while the silica remained as a precipitate. Having diluted the solution, to prevent the destruction of the filter, the whole was now ready for proceeding with the analysis in the usual manner. By this method the work of some hours is accomplished in the course of a few minutes.

The following are the results, which, so far as the sulphur is concerned, are particularly satisfactory:—

	I.	II.
Silica	54·00	53·20
Sulphur	13·23	13·17
Copper	9·30	25·20

To those of your readers who are accustomed to the slow process of oxidation, by digesting with nitro-hydrochloric acid in the usual way, this method will I have no doubt be acceptable.

I remain, Sir,

Douglas, Isle of Man,
April 17th, 1844.

Your obedient Servant,
Geo. Kemp, M.D., Cantab.

Detection of Antimony in cases of Poisoning. By M. Bonjean.

The results deduced by the author from his researches are—

1st. Mineral kermes, administered internally, even in a large dose, is not absorbed like the soluble salts of antimony; probably all the insoluble compounds of this metal are similarly circumstanced.

2nd. In cases of poisoning by an insoluble preparation of antimony, the poison should be especially sought for in the vomited matters, and in those still contained in the stomach and in the intestines.

3rd. To effect the carbonization of organic substances in which the presence of an antimonial compound is suspected, the employment of sulphuric acid alone appears sufficient, under all circumstances, and to be at once the easiest, quickest and most œconomical of all the methods hitherto proposed and adopted.—*Comptes Rendus*, Feb. 22, 1844.

PHARMACOLOGY.

On some new Drugs and their Chemical Constituents. By Dr. L. F. Bley.

Last summer several new drugs were brought from the Port of Valparaiso in Mexico to Hamburg, of which samples were forwarded to me; among them are the following:—

I. *Quillay Bark.*

I received this with the following notice:—"It is the bark of a tree of the same name. It should be left in water one or two days, to soften it, when it is crushed between stones. Mixed with water in this state and stirred, it forms a strong ley, which is especially adapted for washing wool, cloth, silk and linen, and also the hairs of the head. 2 oz. of the bark are said to be sufficient to wash a dress; it is also said to remove all kinds of spots or stains, and to impart a remarkable lustre to the wool."

Dr. Martius, one of our best pharmacologists, informs me "that it is derived from *Quillaia Saponaria* Molin., and is a native of Chili, where it is generally employed for washing. I have been acquainted with this bark two years, and discovered a substance, quillajine, in it, which excites violent sneezing, and is closely allied to saponine, if not identical with it."

Physical Characters.—The bark called Cascara Quillay occurs in pieces of from ten to twelve inches in length and one to one and a half inch in breadth. It possesses a considerable specific gravity, but swims in water, sinking deeply into it; externally it is clothed in some places with a dark brown epiderm, the colour of which inclines at some spots to coffee-brown, at others to brownish-red. This epiderm exhibits numerous horizontal fissures, and appears to be from a half to one and a half line in thickness. Beneath this epi-

derm is situated a whitish-yellow alburnum from one to two lines in thickness; it exhibits only longitudinal fibres, which appear on examination with a magnifying glass to be clothed on the inner surface with a fine short felt. Its colour is yellowish-white, but at some spots it is dull brown or dark yellow beneath the lens, as if impregnated with a resin. Numerous minute bright crystals, probably consisting of the peculiar substance saponine or quillajine, are perceptible with a glass on the surface. This alburnum might be separated without trouble into four thin layers by help of a knife. It is also provided on the interior side with a thin light brown epiderm, upon which some minute crystals are also observed, and indeed, from their darker colour, with the naked eye.

The bark is very brittle; the fracture is very splintery; it is difficult to reduce to a powder, which is of a yellow colour. On pulverization the dust excites violent sneezing, otherwise there is no perceptible odour; the taste is slightly astringent, but very irritating. The bark burns for a short time, not with a very bright flame, leaving a glossy coal, which finally affords a very delicate white ash, which has an earthy, alkaline, and at the same time a slightly sweetish taste. This ash, amounting to about 6·5 per cent., consists of a little sulphate of lime, carbonate of magnesia and lime, chloride of potassium and a trace of phosphates.

Treatment with Water.—1 oz. of the coarsely pounded bark was boiled with 12 oz. distilled water down to 4 oz. In this operation it foamed strongly; the decoction possessed the colour of a warm decoction of brown cinchona bark. This decoction reddened blue litmus-paper, gave with salts of silver a white turbidness and a precipitate, with salts of barytes no opacity, with oxalates a considerable precipitate, the same with nitrate of lead; corrosive sublimate produced a considerable frothing, at first no turbidness, which became evident after long standing, and subsequently formed a slight precipitate; tincture of galls had no effect; solution of perchloride of iron gave rise to a dark colour without any precipitate, tincture of iodine a violet-blue colour, lime water a slight cloudy precipitate. On boiling an ounce of the bark with distilled water as long as anything was extracted, 90 grs. of a strong extract were obtained on evaporation, from which alcohol removed 25 grs. of a substance resembling saponine, which possessed a bright yellow colour and much lustre; it was very brittle when dry, easily broken and reduced to a powder, excited sneezing, was entirely soluble in weak alcohol, had a very pungent taste, and fused readily at the margin on being held over the flame in a platinum spoon; it then swelled without further melting, and left a slight quantity of an earthy ash behind. The remaining aqueous extract afforded gum, with traces of starch, tannine and vegetable salts.

Treatment with Alcohol.—The bark, extracted with water, afforded with alcohol of 0·963 a yellow tincture, which on evaporation left an extract consisting of quillajine and of a yellowish-brown resin, which possessed no peculiar properties. Æther only dissolved a trace of the resin. The quillajine behaves essentially like saponine,

and I consider it as identical, which Dr. Martius is also inclined to admit. The only difference is the greater lustre in external appearance. The amount of this substance however appears to be less than in the German *Saponaria*, and in the Levantine or Egyptian soap root, which is derived from *Gypsophila Struthium*.

The essential constituents of this bark are accordingly saponine or quillajine, gum, small quantities of starch and tannine, fibre and water.

This bark, in my opinion, possesses no advantages over the *Saponaria*. If, on increased importation, the price were to become very low, it might be employed with advantage for washing wool, but medicinally it has no value.

[To be continued.]

On the Hadshy of the Turks. By M. Landerer.

This beverage is derived from *Cannabis sativa*. The relations of climate however produce a far more considerable development of the narcotic principle.

The mode of preparing the hadshy is as follows:—When the hemp plants have blossomed, and have begun to form fruit, the delicate shoots, leaves and unripe fruit are pressed, and set into vinous fermentation by means of a syrup from sweet fruits, or rather are thrown into the fermenting liquid. The fermented liquid is poured into flasks, and frequently coloured red with *Coccus Cacti* or *Coccus Ilicis*, and then used as a spirit.

Another kind of hadshy occurs in the form of an electuarium, which has a very quick but transitory action on the human frame.

It is prepared in the following manner:—Dates, figs, currants and other sweet fruits are pressed to a paste, mixed with fresh hemp and poppy leaves, and formed into balls, which are moistened from time to time with spirits, and preserved in a cool place until they diffuse a strong narcotic odour, which already produces intoxicating effects. This mass is now boiled with butter and oil of sesamum, and the products strained from the residue, poured into tin forms, and placed aside to cool. This is the hadshy of the Arabs, such as is sold in the bazaars of Cairo. It has a greenish-yellow colour, a very rancid taste, and is void of smell.

M. Landerer digested a portion of this hadshy with dilute muriatic acid, and another portion with absolute alcohol. The liquids obtained were yellowish-green, and possessed a very bitter taste. The acid liquid gave voluminous precipitates with alkalies and likewise with tannic acid, which were of a very bitter taste. A concentrated solution of this substance rubbed on the eyelid of a cat, produces in a few minutes a very perceptible dilatation of the pupil; it has likewise the same effect on the human eye. When the hadshy is mixed with water and submitted to distillation, the product obtained has a somewhat bitter taste and a faint odour of herbs. It may be drunk without producing any ill consequences.—Buch. *Rep.*, xxxi. p. 289.

CHEMICAL PREPARATIONS.

Preparation of Benzoic Acid. By Prof. Wöhler.

Pulverized benzoin resin is dissolved, with the assistance of heat, in about an equal volume of highly rectified alcohol, and the solution mixed while hot, but gradually, with so much fuming muriatic acid that the resin begins to be precipitated. The mass is then submitted to distillation. The benzoic acid passes over in the form of benzoic æther. The distillation is carried on as long as the consistence of the mass admits; when it becomes too thick, it is allowed to cool a little, hot water added to it, and again distilled as long as any æther passes over. The water remaining in the retort is, when clear, poured off boiling-hot from the resin; on cooling it deposits benzoic acid, probably derived from benzoic æther.

The product obtained is digested with caustic potash until the whole of the æther is decomposed, finally heated to boiling, and saturated with muriatic acid, when the benzoic acid separates in crystals on cooling.

It appears that the entire amount of benzoic acid of the resin is obtained in this manner; and it may be observed, with reference to the pharmaceutical application, that the acid so prepared possesses entirely the odour of the sublimed acid. Whether the stated proportions of resin, muriatic acid and alcohol are the most advantageous, I am not able at present to say.—Liebig's *Annalen* for Feb. 1844.

Carbonate of Soda in the Preparation of Coffee.

M. Pleischel states from experience, that the infusion of roasted coffee acquires a far superior taste, and is rendered more concentrated, consequently that a much larger amount of beverage can be prepared from the same quantity of coffee, by adding to the boiling water, just before pouring it over the coffee, 1 gr. of crystallized carbonate of soda for every cup, or $2\frac{1}{2}$ grs. for every half ounce of coffee.—*Med. Jahrb. des Oestr. St.*, 1843, October.

On the Decoloration and Blackening of Ointments containing Peroxide of Mercury. By M. Alb. Frickhinger.

All the ointments containing peroxide of mercury lose their colour by keeping; this happens even when the purest peroxide of mercury has been employed; ointments of which wax is a constituent produce this effect most rapidly, and it is advisable, especially with Yve's ointment, to add the oxide of mercury *after* cooling. With ointments into the composition of which no wax enters, it is indifferent whether the oxide is added to the warm fat or not. Sometimes, but more rarely, these mercurial ointments have been observed to become grayish-black, beginning from the surface; this is generally ascribed to the reduction of some mercury from the use of an iron spatula.

The author examined both fresh and entirely decolored, as

well as gray-coloured ointment, and found the peroxide of mercury to have lost in the altered ointments its crystalline structure; but dilute muriatic acid and dilute nitric acid extract from all three both peroxide and protoxide. When the fat was extracted from all three ointments by means of æther (the æther obtained from all deposited with sulphuretted hydrogen a brownish-black coloured fat, containing therefore mercury), peroxide of mercury was first deposited; in each case above it there was in the decolorized preparation a white layer of protoxide of mercury in combination with fatty acids, in the gray one a gray powder of protoxide of mercury; both however still contained peroxide. The author believes that the cause of the blackening is probably owing to the intervention of ammonia.—Buch. *Repert.*, xxxi. p. 305.

Capsulæ gelatinosæ assafœtidæ. *By* O. Schneider.

The complaints of several physicians respecting the difficulties of administering assafœtida internally to patients, especially children, from the odour and taste being so repugnant, has induced me to make some *Capsulæ assafœtidæ* similar to those for *Bals. copaivæ*. For this purpose I form some pills of pure *assafœtida* about 2 grs. in weight, stick them on to needles, and coat them with a solution of Paris gelatine by immersion, and lastly close carefully with a brush the holes left by the needles. Being void of odour or taste, no one has any longer refused to take this medicine, which has since enjoyed in this town (Dresden) a very considerable and successful application. Unfortunately however the preparation is very troublesome and requires so much time as to render it expensive.—*Arch. der Pharm.* Feb. 1844.

Case of Poisoning by Aconitum Napellus. *By* M. Devay.

The subject of this case was a porter in a druggist's shop, who, being hurried at his evening meal, swallowed by mistake, at half past eight o'clock at night, nearly $1\frac{1}{2}$ oz. of an alcoholic solution of aconite, which he had himself placed that morning in a black glass bottle, beside the one containing the wine he used at his meals. He immediately felt a sensation of heat and constriction in the throat, and, alarmed for the consequences, applied, in the absence of his master, to the assistant in the shop, who gave him an emetic, but with hardly any effect. His master, on his return, took him to M. Devay, who found him full of alarm at his situation, complaining of his throat, and of a burning sensation along the course of the œsophagus, and unable to rest in one position. The intellect was entire, there was no disturbance of the senses, the tongue was whitish, there was some nausea but no colicky pains. The effects of the poison were most evident on the organs of locomotion, the lower limbs being incessantly in movement, even during the short intervals when he sat down. From this circumstance he had when walking a peculiar vacillating gait. About $2\frac{1}{4}$ grs. of tartar-emetic with some ipecacuanha were immediately administered in water, which

produced repeated and abundant vomitings. At 11 A.M. the report was as follows:—The patient can no longer keep himself erect; he is seized with convulsive movements, in which the upper and lower extremities are drawn backwards, the fingers being strongly bent over the thumb in the palm of the hand, so that it is impossible to open them; the feet are in a permanent state of adduction; the face is covered with a cold clammy sweat; the eyes turned upwards, so as to leave the whites alone visible, giving a frightful expression to the countenance; no pulsation of the radial and temporal arteries; after continuing about three minutes the convulsion goes off; the patient, whose senses remain entire, except that he is completely blind, is then able to give expression to his sufferings and alarm. At half-past twelve another emetic was given, followed by a lavement, both of which acted freely; drinks acidulated with vinegar were then administered. At 1 A.M. the patient had recovered the sense of vision, but the convulsive paroxysms continued frequent and more frightful than ever; the temperature of the skin was every instant diminishing; shiverings followed, then an icy coldness; the head was thrown strongly backwards; the breathing began to get stertorous, with loud mucous rattle; there was insensibility of the wrists and fore-arms, even to pins being run into them, but the intellectual faculties continued unimpaired. The surfaces of the body were now covered with sinapisms and irritant plasters, and a solution of iodine was given internally. The state now described lasted till 3 A.M.; then symptoms of reaction appeared; the pulsations of the heart and arteries were again felt; and under the use of internal stimuli and warm applications externally, the pulse had, in the course of an hour, risen to 125, the surface being covered with a profuse warm sweat, and sensibility had returned to the wrists. The patient was now out of all danger, and in three days was able to leave his room, without any remaining trace of the effects of the poison, excepting a kind of half-stupid, astonished expression of countenance.—*L'Expérience*, Dec. 1843, as quoted in the *Lond. and Edinb. Month. Journ.*, &c., April 1844.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Observations on African Guano. By W. Francis.

The discovery of considerable deposits of this valuable manure on several small islands off the coast of Africa, where it may be had free of expense, has induced numerous merchants and shipowners to dispatch several vessels for its importation to this country. From one of these, the "Canning," which recently arrived in the port of Bristol, we have received, through the kindness of our friend J. Turner, Esq., a sample, accompanied with the following letter, which, as it supplies some information respecting the localities whence

the article is obtained, will, we doubt not, be read with interest by many of our readers:—

"My dear Sir,

"The sample of African guano which I left with you, and which you have kindly undertaken to analyse, was imported into Bristol, where it is selling at £8 per ton. It is found on several small islands in the neighbourhood of Angra Pequeña, on the western coast of Africa, between 26° and 27° south latitude. The deposit is very considerable, reports say from twenty to thirty feet deep; the sample I sent you was taken up twenty feet below the surface.

"The discovery of these beds will lead to the discontinuance, for the present, of the importation from South America, as the African voyage is performed in half the time occupied by the other; and, moreover, the Peruvian government levy an export duty of £3 per ton, whereas the African is collected without any such payment, there being few, if any, natives in the neighbourhood to interfere with its removal. Already many thousands of tons of shipping have been dispatched to the coast for cargoes, and other vessels are daily departing on the same errand.

"Mr. G. Thompson, of the firm of Borrodaile and Thompson, who travelled in those parts in 1823, describes the natives as 'a tribe of Hottentots called Namaquas; a pastoral people, resembling the aboriginal tribe of the Cape Colony in their general characteristics; living chiefly on milk; addicted to a roaming life; and of a disposition mild, indolent and unenterprising.'

"As regards the probable establishment of trade with the natives, ivory, horns, hides, and perhaps gums, might be obtained from them in exchange for tobacco, beads, &c. The country improves in fertility towards the north, in which direction, at about a hundred miles distance from Angra Pequeña, the Damaras country commences; and Mr. Thompson reports it to be 'very rich in copper ore, which is smelted and worked by the natives.'

"Yours, &c.,

"J. Turner."

The guano, in the state in which it was received, formed a moist chocolate-brown powder, intermixed with numerous particles of a whitish substance. It possessed no urinous odour, but smelt strongly of ammonia. On examination under the microscope, no crystals of any kind could be detected in it; but it contained numerous remains of plants, partly in a state of decomposition, but still exhibiting a green colour, and globules of starch in the cells, likewise brown and white feathers, fragments of egg-shells and fish-bones. The aqueous solution was of a light reddish-brown colour, was strongly ammoniacal, and deposited on slow evaporation an abundant crop of crystals of the triple phosphate of ammonia and magnesia. On adding nitric acid to the filtered liquid, an abundant flocculent brown precipitate subsided, which consisted of humic acid and extractive. The insoluble portion was of a light sandy-yellow colour.

On boiling with solution of potash and precipitation of the filtered

solution with hydrochloric acid, a light brown flocculent substance subsided, which amounted to 5·50 per cent. This was first regarded as uric acid, but on further examination it proved to contain but slight traces of that ingredient, and to consist of a substance allied to humic acid.

To determine the absolute amount of ammonia, one of the ingredients on which the value of guano chiefly depends, a weighed portion of the guano in its normal state was analysed according to the method described by Varrentrap and Will, and afforded 9·70 per cent.

The other ingredients were determined in the usual way, and according to the results of analysis 100 parts of the guano* in question consist of—

Volatile salts, as oxalate of ammonia, chloride of ammonium, carbonate of ammonia, and combustible organic matter, containing 5·50 per cent. humic acid, uric acid and extractive	32·89
Water	27·13
Ammonia	9·70
Phosphates of lime and magnesia	22·32
Insoluble residue in nitric acid, consisting of sand	0·81
Alkaline salts, chiefly phosphates, muriates, and small quantity of sulphates (chiefly potash)	7·08
	100·00

From the above examination, it is evident that the African guano differs considerably from the Peruvian and Chilian, *i. e.* that it has been more exposed to the decomposing influences of atmosphere and water than either of those kinds, and tends rather to confirm the views of Fritzsche, Payen and Boussingault, Girardin and Bidard, that the Peruvian guano is in a state of fossilization.

The most remarkable guano hitherto analysed is that described by Fritzsche†, whose investigations, as far as we are aware, have hitherto remained unnoticed in this country. We need therefore not apologize for giving a brief abstract of them in this place, more particularly as they will prove how requisite it is that the agriculturist, before purchasing guano, should have a sample submitted to analysis by some competent chemist. Fritzsche describes the guano submitted by him to examination as a dry coarse powder, in which

* While drawing up this article for publication, we received from a friend a circular containing an analysis by Dr. Ure of some guano imported by the same vessel, the results of which we subjoin:—

Decayed combustible animal matter, containing 3 parts of uric acid	37·0
Ammonia, chiefly combined with phosphoric acid, only four-tenths being in the state of carbonate	9·5
Earthy phosphates, as above	18·5
Siliceous earth	0·5
Fixed alkaline salts, a good deal of potash salts	6·0
Water or moisture	28·5

These results agree as closely as could be expected in such an heterogeneous mixture.

† *Bulletin de l'Acad. de Petersburg*, I. No. 6.

some large compact masses occurred of a yellowish-brown colour. The compact pieces from which the powder had originated were distinctly composed of superposed strata, seldom horizontal, but most frequently compressed and undulate. The strata are of two kinds, one of a brownish-yellow colour, and consisting principally of urate of ammonia; the other of a blackish-gray or dark brown colour, and formed principally of clay. Both layers alternate with each other irregularly, their relative proportions varying considerably. The argillaceous strata are of a more compact nature than those of the urate of ammonia. All the layers of clay are coated with a whitish rind, which cannot be readily washed off with water This coating consists of urate of ammonia, and proves beyond a doubt that the guano in question has acquired its present state through the agency of water. Feathers, vertebræ and fragments of other fish-bones occur frequently, as well as remains of plants and some seed.

The guano had a strong urinous smell and a faintly saline taste. 16 oz. of the pulverulent mass in its moist state afforded on solution in caustic potash and precipitation with muriatic acid, 7 oz. 2 drms. of a yellowish-brown coloured crystalline hydrate of uric acid = 37 per cent. anhydrous uric acid.

200 grs. of a compact fragment, with very few seams of clay, gave, on being similarly treated, 118 grs. or 59 per cent. of anhydrous uric acid. The residue of these experiments consisted for the greater part of clay, which readily subsided, probably on account of the earthy phosphates contained in it.

From the occurrence of so few organic remains, and from the interposition of the argillaceous masses between the layers of urate of ammonia, it is evident that the guano in question cannot have been deposited by the birds in the state in which it occurs at present; the coating of urate of ammonia, which adheres so firmly to the seams of clay, decidedly shows that water must have acted some part at the formation of this deposit.

Let us suppose a clayey shore, which is flooded at high tide and left dry at ebb, and behind it a lake to which the tide rises, and flocks of sea-birds which visit the coast at the time of low water; all the requisite conditions are given. Fish and other marine animals, left by the tide, attract the birds, which, in taking their food, at the same time loosen the soil. Meantime a tropical sun dries and breaks up the soil; the tide returns, and carries these loose masses of clay, and the excrements deposited on them, into the basin. In their progress a process of lixiviation takes place; the lighter organic remains, which have not time to subside, are carried away by the effluent water, while the heavier urate of ammonia and fragments of clay subside. At some depth the bottom of the basin is not disturbed by the flood, and here a solution of urate of ammonia may be formed, which subsequently, on drying, covers the layers of clay with a white coating, and serves to unite the pulverulent urate of ammonia and loose clay. The amount of soluble constituents in the guano (20 per cent.) is not opposed to this view, for if the urine of these

birds is secreted, like that of serpents, in a concrete form (containing therefore solid urate of ammonia), it would be impossible for the salt water to deprive it of much of its soluble constituents during its transfer, and its rapid subsidence in the basin would prevent subsequent extraction.

Now it is quite evident that the African guano has been exposed to entirely different conditions to that of the Peruvian just described; for while this contains the enormous amount of 59 per cent. uric acid, scarcely traces of it occur in the former, it having undergone total decomposition. Moreover, the amount of soluble constituents in the African guano (above 60 per cent.) entirely excludes all idea of its having been subjected to any such lixiviating process as that supposed by Dr. Fritzsche.

We may, in conclusion, venture a few words with respect to the comparative value of the African guano as a manure. This depends, first, on the amount of phosphates, and secondly, on that of the ammonia, or substances capable of affording that ingredient. But it is also evident that the state in which the nitrogenous compounds are contained in the manure must be of some importance, *i. e.* whether they exist in the form of ammonia, as is the case with the guano submitted by us to analysis, or in the state of uric acid *.

It is probable that this African guano would prove extremely stimulating to vegetation at first, but that its power would soon be spent, unless previous to its employment it were mixed with some substance capable of fixing the ammonia, such as gypsum or charcoal, as recommended by Boussingault and Payen; while that containing uric acid would, from the slow decomposition of this substance, prove for a long time a constant source of nitrogen proportionate to the growth of the plants.

Preparation of Varnish.

Take dry pulverized sulphate of lead, rub it up with linseed oil, and pour so much linseed oil over it that when shaken the whole acquires a milky colour. The shaking is repeated several times in the course of three or four days, and the vessel placed in a situation exposed to the light. The sulphate of lead subsides, carrying down with it a portion of the mucus from the oil, which at last becomes quite clear, and in the course of time is entirely bleached. The mucus above the lead sediment forms a compact membrane, which becomes so hard that the supernatant clear oil may be poured off. The lead sediment may be preserved and used repeatedly, having

* "The value of a manure depends therefore on the proportion of nitrogenized organic matter, and especially in relation to the non-nitrogenous organic substances, and lastly, on the decomposition of the quaternary substances being gradually effected, and so keeping pace with the progress of vegetation." And again, "A manure entirely decomposable into its soluble and gaseous products in the course of a single year will be capable of producing as great an effect on the first crop as five times the quantity of another manure which would require five years for its ultimate decomposition, but then the latter will furnish useful products during a period five times longer."—*Payen* and *Boussingault* in *Ann. de Chim. et de Phys.*, t. iii. pp. 67 and 70.

removed the mucous deposit from it. This varnish dries quickly, and can be employed for lac colours. At all events its application is more to be recommended than such as contain sugar of lead, white lead, and other useless and injurious admixtures. Since the manufacture of this varnish is as cheap as it is simple, it might easily be executed on a large scale.—*Preuss. Gemeinnütziges Volksblatt.*

PATENTS.

Patent granted to Charles Köber, Leeds, *for Improvements in fixing Colour in Cloth.*

This invention consists,—1st, in the use of bichromate of potash as a medium for uniting the colouring ingredients used in dyeing with the wool, whereby a faster, brighter and cheaper colour is obtained, and is more effectually fixed in the cloth than by using the mordants generally employed, such as sulphate of iron and sulphate of alumina and potash, or, as they are commonly called, copperas and alum.

In consequence of the great affinity of bichromate of potash for the wool, as well as for the colouring ingredients, a comparatively small quantity of it will fix the dye-wares; that is to say, 1 lb. of bichromate of potash can be used instead of from 3 to 4 lbs. of alum or copperas; besides which, the colour produced by the use of bichromate of potash is fast in alkalies and air, and better resists the operations of scouring and the milling process employed in the manufacture of cloth; and less colouring ingredients are required to be used than by the ordinary mode, because the colour produced thereby being faster, no loss of colour will take place when scouring the cloth with soap; and the fibres of the wool, in the dyeing of which bichromate of potash is employed, will not be injured, as they have hitherto been, by the acids contained in alum or copperas; and, on the contrary, the cloth will be softer and easier to be scribbled and milled, and consequently the same quantity of wool will produce a greater and better quantity and quality of cloth than by the method usually employed.

The ordinary colouring ingredients are employed in conjunction with the bichromate of potash; and as every different shade and colour requires a different proportion of ingredients, and the dye-wares differ so much in quality that sometimes a double quantity of them is required, it is impossible to state the different proportions in which the bichromate should be used with them, the requisite amount varying according to the quantity of ingredients to be fixed in the wool; but the patentee generally employs 3 lbs. of bichromate of potash for preparing 100 lbs. of scoured wool, and he sometimes adds 2 lbs. of argol or tartar. In this liquor, thus produced, the wool is boiled for one hour and a half, and on the next day the colour is filled up with as much of the colouring ingredients as the desired shade may require.

The second improvement consists in obtaining green colours perfectly fast in acids, alkalies and air, by dyeing the wool blue, and then manufacturing the cloth from the blue wool, so as to make it what is called partly finished cloth, with a white or coloured list, and then adding the yellow wares or ingredients to the cloth, instead of to the wool; by which means a perfectly fast green colour will be obtained, similar in appearance to wool-dyed green, but much faster. Every kind of yellow ware may be used, but fustic is preferred; and in order to fasten the colour, hydrochloric acid saturated with tin is used, to which is added as much water as will give the solution a specific gravity of 1·2612, or 30° Baumé; and of this solution from 6 to 7 lbs. is used for every 100 lbs. of cloth, besides the usual quantity of alum and argol. This solution could not be applied to wool in fleeces, as it would be destructive to the use of soap, and consequently to the milling process.

The last part of this invention consists in the use of soda and bran for dissolving the indigo in the vats for dyeing blue, whereby the indigo is better fixed in the wool, and at a less expense than is incurred by the use of woad, madder and bran, which are usually employed for that purpose.

The soda is employed in the following manner:—In a seven feet vat the water is heated to 125° Fahr., and 65 lbs. of bran, 35 lbs. of common soda (which has about 23 per cent. of carbonate of soda), and 4 lbs. of indigo are thrown into it, together with the same quantity of lime as is usual for woad vats. The vat is worked from 110° to 118° Fahr., three or four times during the day, without stirring; and in the evening the vat is heated to a temperature of 125°, and into it is thrown about 4 lbs. of lime, 6 lbs. of bran and 5 lbs. of soda, with such an additional quantity of indigo as may be required for the following day; after this addition the vat is stirred as usual. If the vat has been working during the day, the above quantity of lime, bran and soda is added every evening, together with the requisite quantity of indigo. It would be difficult to state the exact quantity of indigo required, as any amount from $\frac{1}{2}$ a lb. to 25 lbs. may be added, according to the shade of colour required to be produced the following day. After proceeding in this manner for eight or ten weeks, the sediment is removed, and, with the liquor in the old vat, the operator sets a new vat, adding 13 lbs. of bran and 10 lbs. of soda, with as much lime and indigo as may be required. The use of lime being to check the fermentation produced by the bran, it is impossible to state the exact quantity which may be required; but enough is used to check the fermentation in the vat to such a degree as will be sufficient to deprive the indigo of its oxygen without an immoderate fermentation, which is very prejudicial. The vat in which the soda is used must be perfectly yellow, that is to say, the indigo must be perfectly deprived of its oxygen, or, as it is generally termed, the indigo must be "sprung," in which case the vat appears yellow. By the use of soda ashes (which have about 46 per cent. of carbonate of soda) instead of common soda, half the quantity will produce the same effect. Pearlash may likewise be employed

if the price will admit of it, and fine sharps may be used instead of bran.—Sealed March 7, 1840.

Patent granted to Richard Archibald Brooman, London, *for the Manufacture of Paper, Cordage and other textile Fabrics, from certain Vegetable Matters, and for the Application of the said Materials.*

The first part of this invention consists in manufacturing paper, cordage, matting and other textile fabrics from the *convolvuli* of the *Cistus* genus or family of plants, abounding in English, French and Dutch Guiana, the West India Islands, the Brazils, on the coast of Africa, and other parts. All the plants of this order may be used; but the *Mimosa scandens*, the *Guidandina bandue* and the *Ledum*, or marsh bindweed, are preferred.

The stems of these plants are stripped of the bark, and beaten or bruised to separate the fibres, which are then dried, for the purpose of extracting the sap, and afterwards boiled for three or four hours with a suitable quantity of American potash. After this the fibres are washed, and then bleached by immersion in hydrate of chlorine for three or four hours, or by any other means; and if a greater degree of whiteness should be required, they are next boiled with soda, washed and steeped in water saturated with slaked lime. The fibres are then combed with a metal comb, and reduced by pounding to a pulp, which is ready to be made into paper in the ordinary way, either alone or in combination with any other material.

The bark of these plants may be also converted into pulp by the above processes, the epidermis or outer covering being first removed. The plants known in the West India islands by the name of *herbes coupuntes*, and the bark of the West India pear-tree (*poirier*) may likewise be rendered suitable for making paper, by operating upon them in the manner above described, but omitting the combing process.

The plants are prepared for making cordage, matting and other textile fabrics, by reducing them to filaments in the above manner, then soaking, and afterwards submitting them to the same processes which hemp and flax undergo. The second part of the invention consists in employing the fibres of the above plants for stuffing cushions and mattresses, after they have been treated in a manner similar to that described for making paper, except the bleaching process, which is in this case unnecessary.—Sealed Aug. 10, 1843.

THE CHEMICAL GAZETTE.

No. XXXVIII.—May 15, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Transformation of Fibrine into Butyric Acid.

By Ad. Wurtz.

When fibrine is exposed to the air during the heat of summer, it becomes entirely converted into a liquid in the course of eight days, which diffuses an odour of putrid cheese and is coagulated by heat. This last property is due to the albumen which it contains, and which may be easily isolated by precipitating the liquor, diluted with water and filtered, with the subacetate of lead, washing the deposit and decomposing it by a current of carbonic acid. A solution, coagulable by heat, is thus obtained, which presents all the characters of albumen. The other products of this putrefaction are carbonic, acetic and butyric acids, and ammonia.

In order to isolate the butyric acid, I diluted the liquid arising from the putrefaction of the fibrine with twice its volume of water, heated the liquor, and added sulphuric acid in slight excess. The precipitated albumen was separated by filtration, and the clear liquor distilled to within half its volume. The product of distillation reddened blue litmus-paper strongly; it was neutralized with carbonate of lead and the solution evaporated. At a certain degree of concentration butyrate of lead separated from it in the form of a thick oil, which changed into a soft and resinous mass on the cooling of the liquid. This was decanted, evaporated to dryness, then redissolved in alcohol. The alcoholic solution, having been mixed with water, became turbid, and deposited a fresh quantity of butyrate of lead, offering the characters which I have just indicated. This salt was redissolved in weak alcohol, and decomposed with a sufficient quantity of caustic potash. The filtered liquid was evaporated nearly to dryness, then treated with concentrated phosphoric acid, which separated an oily layer from the liquor, which was removed in order to submit it to distillation. The point of ebullition of the acid rose rapidly from 266° to above 320°, and the product of distillation, which was quite colourless, presented all the characters of butyric acid.

Putrefaction is not the only way in which fibrine is transformed into a fat volatile body. I have observed that by heating pure fibrine with potash-lime in an oil-bath at a temperature of from

320° to 356°, a small quantity of a volatile fat acid forms, which remains in combination with the potash, whilst ammonia and other volatile products are disengaged. It is easy to extract the volatile fat acid from the residue, by dissolving this in water, supersaturating with phosphoric acid, and submitting the liquid to distillation. The distilled product is neutralized with an alkali, evaporated, and the residue treated with syrupy phosphoric acid, which separates an oily layer from it, easily recognised as a volatile fat acid. This acid possesses the properties of butyric acid; I have however not yet verified its identity with this acid by analysis.—*Comptes Rendus*, April 15, 1844.

On Zircona and some of its Salts. By R. Hermann.

The author gives the preference to Wöhler's method of fusing finely-pulverized zircons with hydrate of soda. He redissolves the hydrate precipitated from the muriatic solution by ammonia in muriatic acid, allows the basic salt to crystallize from it, washes with alcohol, recrystallizes from water, and then precipitates the zircona from the solution of the perfectly white crystals by ammonia. When the zircons or hyacinths employed are not very pure, it is best not to allow the muriatic solution of zircona to crystallize, but to add immediately an excess of crystallized sulphate of potash to the liquid filtered from the silica, to boil, and pour while hot from the undissolved sulphate of potash, then place aside to cool, when the basic sulphate of zircona separates. It is filtered, and a fresh quantity of the basic salt obtained from the mother-ley by neutralizing with carbonate of potash, and treating it again with sulphate of potash. The basic salt is then fused with twice its weight of hydrate of soda, the mass extracted with water, the residue dissolved in muriatic acid, precipitated by ammonia, well edulcorated, re-dissolved in muriatic acid, and recrystallized several times.

When zircona is precipitated by fixed alkalies, it enters into combination with a portion of the alkali, which cannot be removed by washing. Such a compound, differing by its greater whiteness, and by the absence of the luminous phænomenon, on ignition, from pure zircona, contained 3·11 per cent. potash. Other metallic oxides, such as oxide of copper, oxide of silver, &c., likewise enter, when present in the solution, into the composition of the precipitate, and cannot be removed from it by an excess of ammonia.

Hydrate of zircona, dried at 64° Fahr. over sulphuric acid, contained, according to the author, 22·89 water; the formula $Zr^2O^3 + 3HO$ requires 22·83. The hydrate examined by Berzelius contained only half that amount of water, and therefore must have been dried more strongly. *Anhydrous zircona* contains, according to the analysis of the chloride of zirconium, 26·52 per cent. of oxygen. Zircona is considered, according to analogy, from the chloride being volatile and the fluoride of zirconium being readily soluble in water, to be Zr^2O^3; and we have therefore—

Zr.....	73·48	2 =	840·4	73·69
O.....	26·52	3 =	300·0	26·31
			1140·4	

The atomic weight is that deduced from experiments by Berzelius. The author found chloride of zirconium, Zr^2Cl^3, to contain 61·5 per cent. chlorine (atomic weight for zirconium equal 831·30), while basic muriate of zircona ($2Zr^2O^3 + 3ClH$) contained, according to two analyses, 37·544 and 37·220 per cent. muriatic acid; whence we have 1135·65 and 1151·4 as the atomic weight of zircona. Berzelius's determinations by means of sulphuric acid vary between 1138·73 and 1142·04. The number 1140 therefore very well represents the mean of all experiments.

Carbonate of Zircona.—When a solution of a neutral alkaline carbonate is added to a neutral solution of a salt of zircona, the first portions produce no change in the liquid; on further addition carbonic acid escapes with effervescence. The alkali of the carbonate salt seizes hold of a portion of the acid of the zircona salt, producing a soluble basic salt of zircona and free carbonic acid. On further addition of carbonated alkali, the liquid becomes turbid, with separation of hexabasic carbonate of zircona. This precipitate increases until the whole of the zircona has separated. If we now continue the addition of carbonate alkali, the precipitate gradually redissolves, and after the addition of twice the quantity of alkali as was requisite to precipitate the whole of the zircona, the liquid is again rendered perfectly clear. In this case therefore a soluble double salt is formed of hexabasic carbonate of zircona, probably with bicarbonated alkali, perhaps according to the formula $(2Zr^2O^3, CO^2) + RO, 2CO^2$. These phænomena result whether neutral sesquicarbonate or bicarbonate alkalies are employed, as in all cases the quantity of bicarbonates in the liquid requisite for the formation of double salts can be produced from the eliminated carbonic acid. It is likewise indifferent whether carbonate of potash, soda or ammonia is employed to saturate the solution of carbonate of zircona. But if the salt of zircona was not pure, if the zircona contained but a small quantity of alumina, titanic acid, &c., the precipitate dissolves only to a very slight extent in the excess of carbonate alkali. This circumstance prevents, in most cases, the otherwise characteristic behaviour of the carbonate of zircona towards carbonate alkalies being employed for analytical purposes. Hydrate of zircona does not dissolve in carbonate alkalies, even in the recently-precipitated state.

Recently-precipitated hexabasic carbonate of zircona forms a white flocculent precipitate, and on drying, white cohesive pieces. When boiling water is poured over moist carbonate of zircona, the carbonic acid escapes with effervescence; and in like manner it parts with a portion of its carbonic acid on drying in a warm situation, and entirely at a faint red heat. It is therefore requisite, in order to obtain it dry, to wash it with cold water, and to dry it, at first by exposure to the air, and subsequently at 64° Fahr. over

sulphuric acid. Carbonate of zircona, prepared in this manner, consisted of—

Zircona.....	70·84	2	70·60
Carbonic acid	8·13	1	8·51
Water	21·03	6	20·89
	100·00		100·00

Phosphate of Zircona.—When free phosphoric acid is added to a solution of a salt of zircona, sesquiphosphate of zircona separates as a slimy transparent precipitate, resembling that of alumina, which dries to a transparent mass, like the hydrate of zircona. Phosphate of zircona is not wholly insoluble in the free acid, for a considerable precipitate of the phosphate of zircona is obtained on adding ammonia to the acid liquid, from which the phosphate had been separated by free phosphoric acid. The neutral alkaline phosphates produce, in a solution of a salt of zircona, the same compound as free phosphoric acid.

Phosphate of zircona, precipitated by neutral phosphate of ammonia from sesquimuriate of zircona, consisted of—

Zircona.....	45·78	2	46·00
Phosphoric acid	54·22	3	54·00

Sulphate of Zircona.—The author adds a hexabasic sulphate of zircona to the three sulphates described by Berzelius. This salt is formed on mixing a concentrated solution of a salt of zircona with a boiling saturated solution of sulphate of potash. On the cooling of the mixture, it separates as a flocculent white precipitate, forming when dry white coherent fragments. It is insoluble in a solution of sulphate of potash, but dissolves in considerable quantity when washed on the filter with pure water. In this case a soluble salt of zircona with more acid is formed, while a still more basic compound remains on the filter. The salt consisted of—

Zircona.....	81·55	6	81·99
Sulphuric acid.....	18·45	3	18·01

The formation of this compound depends on the tendency of the sulphate of potash to form bisulphate, and on that of the zircona to form a basic salt. The hexabasic sulphate of zircona contains, when it has been prepared with sulphate of potash, a small quantity of the latter, which does not belong essentially to the composition of the salt.

Sulphite of Zircona.—Solutions of salts of zircona behave toward sulphite of ammonia precisely in the same manner as towards carbonate of ammonia. When solutions of the two salts are mixed, a precipitate of basic sulphite of zircona is at first formed, but on further addition of sulphite of ammonia it redissolves. On boiling this solution sulphurous acid escapes and hydrate of zircona separates. It is moreover remarkable that the solution of sulphite of zircona in sulphite of ammonia is not decomposed by caustic alkalies; the liquid remains as clear after the addition as before. If the zircona contain peroxide of iron, this is at first precipitated by sul-

phite of ammonia in company with the zircona, and on further addition is redissolved along with the zircona. On boiling this solution, hydrate of zircona, contaminated with peroxide of iron, is precipitated. Dissolved in sulphite of ammonia, the oxide of iron cannot be separated by caustic alkalies from the zircona; both remain in the solution: the sulphite of ammonia prevents therefore, like many organic substances, the precipitation of the zircona and of the peroxide of iron by caustic alkalies. The iron however is thrown down from this solution by hydrosulphates as sulphuret of iron.

Chloride of Zirconium is obtained by heating to redness a mixture of zircona or pulverized zircons with charcoal, in a current of dry chlorine gas. A porcelain tube, half filled with the above mixture, is connected with an apparatus for disengaging chlorine, and raised to a moderate red heat. Chloride of zirconium sublimes into the cooler portion of the tube, and must now and then be removed. It forms a white saline mass, which fumes when exposed to the air, and produces when brought on to the tongue a sensation similar to that of red-hot metal. Thrown into water, it hisses like red-hot iron, and dissolves readily and entirely. On evaporation half the muriatic acid escapes, and sesquimuriate of zircona separates in crystals.

The chloride of zirconium consisted of—

Zirconium	38·50	2 =	840·40	38·75
Chlorine	61·50	3 =	1327·95	61·25
	100·00	=	2168·35	100·00

Bibasic or Sesquimuriate of Zircona is obtained either by dissolving chloride of zirconium in water and driving off the liberated muriatic acid, or by dissolving hydrate of zircona in an excess of muriatic acid and evaporation. In both cases the same compound crystallizes. It has hitherto been erroneously considered as the neutral muriate of zircona, which does not exist, for the half of the muriatic acid is expelled on dissolving the chloride of zirconium in water and evaporation. The sesquimuriate of zircona crystallizes readily in white silky prisms, generally in stellate groups; they are easily soluble in water and in alcohol; the solutions have an astringent taste.

The hypothetical dry salt consists of—

Zircona	62·456	62·78	2	62·55
Muriatic acid ..	37·544	37·22	3	37·45

The crystallized salt contained 42·02 per cent. water (24 atoms = 42·52).

Terbasic Chloride of Zirconium with Oxide of Zircona.—This compound is obtained on gently heating the crystallized sesquimuriate of zircona; water and muriatic acid are expelled; the crystals become opake, white and insoluble in water, without losing their form. The compound contained 30 per cent. chlorine.

Nitrate of Zircona.—The mass obtained by dissolving hydrate of zircona in excess of nitric acid, and evaporation by exposure to the

air, appears to be the neutral salt Zr^2O^3, $3NO^5$. If it be dried at 212°, it leaves a saline mass, which is readily soluble in water and in alcohol, and contains only 52·45 per cent. zircona, therefore $= 2Zr^2O^3 + NO^5$. By repeated solution and evaporation of this second salt, it parts with still more nitric acid, and at last a gummy mass is obtained with 64·59 per cent. zircona, which nearly corresponds to the formula $3Zr^2O^3 + 3NO^5$.—*Journ. für Prakt. Chem.*, xxxi. p. 75.

Observations on the Bile. *By* Dr. Kemp.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,

In your Journal, dated Oct. 16, 1843, I called the attention of your readers to the fact, that my analyses of the ox-bile had been misstated by Prof. Liebig in a paper contained in the 'Annal. der Chem. und Pharm.' for July, and of which you gave a translation in the 'Chem. Gaz.' for October 1st of the same year.

It was at that time my intention to solicit a place in your Journal for my corrections; the subject however required a much more lengthened and detailed consideration, and I found that it would have been impossible, with any justice to the subject, so far to condense my statement as to render it suitable for a periodical. I much regret that the paper of Messrs. Theyer and Schlosser, which appeared in No. 37 of your Journal, did not reach me before I published my letter to Liebig, as it would have furnished me with additional confirmation of the facts which I have now repeatedly, and in different ways, brought before the public.

In your introduction to the researches of MM. Theyer and Schlosser you remark, "The facts contained in this article are further confirmations of the circumstance pointed out by Liebig, viz. that biliary matter, freed from mucus, fat and colouring matter, is really nothing more than bilate of soda; and that Thenard's picromel, Kemp's bilic acid, Demarçay's choleic acid, Berzelius's bilifellinic acid, and the organic substance contained in addition to soda in biline, are in reality the same organic acid, but which, on account of their ready decomposition, are difficult to obtain pure." Now that the biliary matter of the ox is bilate of soda, was shown, not by Prof. Liebig, but by my researches at Giessen, conducted without his assistance or presence, as at the time the fact was decided he was in England; and that he is indebted to me for his information on this subject I can prove from his own correspondence, as well as the priority of my publications. With reference to the proof of identity between the electro-negative organic body in the bile and the other bodies mentioned, I can only briefly observe, that the picromel of Thenard differs essentially from that body in its physical characters; that until the bilifellinic acid of Berzelius has been submitted to ultimate analysis, all comparison between it and other bodies must be mere speculation; and that the choleic acid of Demarçay is as perfectly distinct from the organic body in the ox-

bile as both chemical and physical characters can render it; the combining weight, relative proportion of ingredients, solubility in water, and general behaviour towards reagents, furnishing us with an unusual accumulation of means whereby to discriminate the two.

With the exception of one or two immaterial errors, which would be invidious for me to point out, and which do not at all affect the general issue, it will be seen that the researches of MM. Theyer and Schlosser, with which you have now favoured us, are identical with, and in the strongest manner confirmatory of, my views, as opposed to those of Prof. Liebig, putting it beyond question that his formula for the organic portion of the ox-bile, viz. $C^{76}\,H^{66}\,N^{2}\,O^{22}$, is quite untenable, and bearing no relation to that deduced in the ordinary manner from my researches, and the subsequent confirmations of them in the paper before us.

The formula I proposed for the organic matter in ox-bile, obtained in the usual manner, is $C^{48}\,H^{42}\,N\,O^{13}$. By proceeding in the same way with the bilate of soda of Messrs. Theyer and Schlosser, we also obtain* $C^{48}\,H^{42}\,N\,O^{13}$, a coincidence which, it is needless to say, could not be accidental; and I do think that Prof. Liebig is now bound to make the *amende honorable* by retracting all that portion of his work on Animal Chemistry which relates to the composition and uses of the bile; for not only are his notions with respect to the ox-bile incorrect, but the ox-bile is not *human* bile, and all his deductions on that subject must be unequivocally rejected as unsound.

With reference to the lead salts of bile, or rather the action of the salts of lead on bile, I think we are at present not in a condition to decide, as with every precaution we are never secure of uniform results. The same may be said of metallic oxides generally, almost every one of which I have tried.

A very interesting product of oxidation is effected by the action of nitric acid on the bile, freed from mucus, fatty acids, &c., and the examination of this body will no doubt be important. I gave the portion I formed at Giessen to Dr. Enderling, but am not aware that it has been analysed.

I remain, Sir,

Douglas, Isle of Man,
May 6th, 1844.

Your obedient Servant,
Geo. Kemp, M.D., Cantab.

Observations on M. Langlois's new Acid of Sulphur. By H. Rose.

This acid is generated when a solution of bisulphite of potash is digested with sulphur at a very gentle heat; besides sulphite of potash nothing further is formed than the potash salt of the new acid. Now it is not seen what part the sulphur acts in this reaction, for the constituents of the bisulphite of potash are alone sufficient to form these products, for $2\,(KOS^{2}O^{2}) = KOSO^{3} + KOS^{3}O^{5}$. M. Rose observes, that anhydrous sulphite of ammonia undergoes a similar

* Taking the combining weight as 5600.

decomposition on being treated with water. Some time ago he showed that ammoniacal gas combined only in one proportion with sulphurous acid gas, forming anhydrous bisulphite of ammonia, $NH^3 + 2SO^2$, which on solution in water is decomposed into sulphite of ammonia and into the ammonia salt of the new acid, which has been very properly designated by Berzelius trithionic acid.

M. Rose then observes, that trithionates may very probably originate in many other cases, as for instance in the treatment of chloride of sulphur with water, since sulphuric acid is always formed in this reaction, even when the chloride of sulphur contains an excess of sulphur in solution; and likewise when the combinations of chloride of sulphur, SCl^2, with certain chlorides, such as chloride of tin ($SnCl^2 + 2SCl^2$), are placed in contact with water.—*Proceedings of the Royal Academy of Berlin*, Jan. 8, 1844.

Hyperoxide of Chromium.

When, according to M. Krüger, the hydrate of the oxide of chrome is heated strongly, but not to redness, with access of air, it parts with its water and becomes brown. When the brown powder is heated to redness, it gives off the absorbed oxygen with most violence at the moment of the peculiar luminous phænomenon; it is then green. When hydrate of the oxide of chrome is heated to redness in carbonic acid or nitrogen gas, no luminous appearance occurs; this however is very apparent in an atmosphere of oxygen gas. The hyperoxide dissolves in hot muriatic acid with liberation of chlorine; it is insoluble in dilute nitric acid and in caustic potash even on boiling, and remains quite unchanged.—Poggendorff's *Annalen*, lxi. p. 219.

On the partial Reduction of the Binoxide of Copper by Heat, and on the new Oxide which results. *By* MM. Favre and Mamené.

From the experiments detailed in this memoir it results, that when the binoxide of copper is decomposed at a temperature approaching to that of the fusion of copper, it melts, losing eight-hundredths of its weight of oxygen, and is converted into a body which is represented by the formula $Cu^5 O^3$. This new oxide is readily distinguished, even by its physical properties, from the body whence it is derived. Its surface is of a black colour, from its absorbing oxygen on resuming the solid form; but its fracture is reddish, and when reduced to a powder it becomes almost as red as the protoxide of the same metal. It is hard and brittle.—*Comptes Rendus*, April 8.

On the Amides which originate from the Action of Ammonia on Fat and Oils, especially on Margaramide. *By* M. Boullay.

The action of ammonia on fats is totally different from that of the fixed alkalies. According to the author, amides of the fat acids are

formed. If we consider this in connexion with the few experiments which we possess, by Bonaster and Dumas on oil of cloves and oil of cinnamon, by Dumas and Pelouze on oil of mustard and oil of bitter almonds, by Cahours on oil of carraway, oil of cinnamon and oil of gaultheria, with respect to their behaviour towards ammonia, the action of ammonia on the fat and essential oils contained in plants appears to act an important part in the formation of the amidogenoid vegetable substances, especially of the alkaloids.

The author first operated upon olive oil and pork fat, and saponified these either by means of a current of ammoniacal gas, or by mixing with an alcoholic solution of ammonia, or lastly, by leaving them in contact for a long time with an aqueous solution of ammonia. The soap has at first an alkaline reaction, but if it be warmed at 86° Fahr. until no more ammonia escapes, it becomes perfectly neutral. It may be divided in boiling water, but does not dissolve; on cooling, the greater portion solidifies on the surface, while glycerine, colouring substance, and the acid salt of ammonia of an acid which is precipitated by acetate of lead and nitrate of silver, but not by lime and barytes, remain dissolved in the water. If the separated solid substance is dissolved in boiling alcohol, and the solution set aside to cool, a white, crystalline, perfectly neutral substance separates, while small quantities of margaric and oxalic acids remain in the mother-ley. The substance, purified by repeated crystallization, melted and dried in the water-bath, is pure margaramide; it is white, solid, perfectly neutral, readily soluble in alcohol and æther, but not at all in water. It separates from the hot solutions on cooling in needles or warty transparent masses. It melts at 140° Fahr., and burns like fat with a luminous flame, leaving no carbonaceous residue. Dilute solutions of potash, soda, lime and barytes do not act upon it; but when boiling and concentrated, they disengage ammonia and leave behind a salt of margaric acid. Acids act likewise only when concentrated, and especially when warm. Margaramide consists of—

Carbon.....	75·68	75·81	34	75·8
Hydrogen	13·05	12·88	35	13·0
Nitrogen	5·33	5·31	1	5·2
Oxygen	5·94	6·00	2	6·0

The formula is therefore $= C^{34} H^{33} O^2, NH^3$, *i. e.* anhydrous margarate of ammonia minus 1 equiv. of water.

Oil of almonds, rape oil, nut oil and poppy oil afforded perfectly analogous results; castor oil is peculiar, from the rapidity of the action and the remarkable products.—*Comptes Rendus*, xvii. p. 1346.

Pyrophorus from Chromate of Lead.

When, according to M. Anthon, neutral chromate of lead is mixed with a quarter to one-eighth of its weight of sulphur, the mixture rubbed together with some water, and formed into small pellets, which are dried and heated to redness in a glass tube as long as any sulphur is given off, a product is obtained which burns brilliantly on

exposure to the air with evolution of sulphurous acid. The ignited pellets part with much oxide of lead at the ordinary temperature to acetic acid, become of a lighter colour when treated with concentrated nitric acid, and on boiling liberate hyponitric acid, and the acid then contains protoxide of chromium and oxide of lead. It is evident therefore that some sulphuret of chromium has formed by the action of the sulphur at a red heat on the chromate of lead.—Buchner's *Repert.*, xxxi. p. 358.

ANALYTICAL CHEMISTRY.

Method of distinguishing between the various kinds of Starch by means of Iodine. *By* M. Gobley.

The author places the starch in watch-glasses under a bell-glass containing iodine, and leaves them exposed there for four-and-twenty hours, when the granules acquire the following colourings:—

Wheat-starch	Violet.
Potato-starch	Dove-gray.
Genuine arrow root	Bright chocolate colour.
Arrow root with ¼ wheat-starch	Grayish-lilac.
Manufactured arrow root	Dove-gray.
Genuine tapioca, entire	All the granules yellowish.
... ... pulverized	Chamois colour.
Pulverized tapioca mixed with ¼ wheat-starch	Violet.
Spurious tapioca, entire	Some granules of a violet-gray, others yellowish.
... ... pulverized	Chamois colour.
The same with ¼ wheat-starch	Violet.
White sago, entire	Some granules of a violet-gray, others yellowish.
... ... pulverized	Chamois colour.
The same with ¼ wheat-starch	Violet.
Spurious sago, entire	Some granules violet-gray, the others yellowish.
... ... pulverized	Chamois.
The same with ¼ wheat-starch	Violet.
Dextrine	No colouring.

From the above it will be seen that wheat and potato-starch acquire, under the influence of iodine vapour, a widely different colouring; that arrow root, which when pure assumes a light chocolate colour, becomes of a lilac-gray when mixed with ¼ wheat-starch; and that spurious arrow root assumes a dove-gray colour, that is to say, the same colouring as the potato-starch from which it had been prepared; that the tapiocas and sagos, entire, genuine or spurious, acquire the same yellowish tint; that the powders, genuine and spurious, all acquire a chamois colour.

Thus it is possible, by means of iodine vapour, to distinguish between wheat and potato-starch, genuine arrow root from spurious, or when mixed with wheat-starch. It is also possible to determine whether the tapioca powders, genuine and spurious, have been replaced by corn or potato-starch, or have been mixed with them; but it will be impossible to decide whether manufactured tapioca and sago powders have been substituted for genuine.

The colouring of the starch granules is owing to the property which these bodies possess of absorbing the vapour of iodine and water. Experiment shows that these granules are not coloured by iodine unless moist. When they have been dried at 212°, they absorb iodine, it is true, but only become coloured on recombining with water.—*Journ. de Pharm.* for April 1844.

PHARMACOLOGY.

Further Experiments on Radix Sumbul. *By* H. Reinsch.

The author has completed his general analysis of this root, communicated in a former Number*, by a more accurate examination of the balsamic constituents. He extracted the root with boiling alcohol of 84 per cent., distilled the alcohol from the extracts, and exhausted the residue with æther; on removing this by distillation, the balsam remained behind of a brown colour.

It is obtained in a purer state by immediate extraction of the root with æther. The portion of the alcoholic extract insoluble in æther contains,—beside sugar, colouring substance and a nitrogenous body, —the bitter substance of the root, which is soluble in water and in alcohol, and subsequently proved to be a balsam contaminated by several other substances.

The balsam was dissolved in caustic potash and boiled for some hours, when water and some essential oil distilled over. On dilution with water, a tenacious precipitate formed in the alcoholic solution, which was separated and washed with water. The brown filtered solution deposited, on treatment with dilute sulphuric acid, a dark brown oil in small quantity, which possessed an odour resembling creosote and a very pungent taste. On distilling it with water, some drops of oil and some minute laminæ and acicular crystals were obtained, which latter subsided in the acid aqueous distillate, which possessed an aromatic odour. After long standing more crystals separated from the liquid, which were then removed. The liquid saturated with ammonia was not altered by salts of the earths, tartar-emetic, nor by acetate of lead. It was precipitated white by basic acetate of lead, reddish-white by acetate of the peroxide of iron, white and crystalline by nitrate of silver, and afforded, after some time, blue laminæ with acetate of copper.

The crystals resemble crystallized acetic acid; when moist have an acid aromatic odour, which is very faint when they are dry; they possess a burning acid taste, dissolve slightly in water, to which they

* See p. 68.

communicate an agreeable aromatic taste, dissolve readily in alcohol and æther, melt easily, sublime without being decomposed, and burn with a luminous flame. Their alcoholic solution is rendered blue by sulphuric acid; their combination with ammonia gives off a saffron-like odour; they expel carbonic acid from carbonate of soda, producing a deliquescent crystalline salt. Only 10 grs. of this acid were obtained from $1\frac{1}{2}$ oz. of balsam, the product of 17 oz. of dry root. The author calls the acid separated from the oily portion of the Sumbul balsam, Sumbulolic acid, and the previously-obtained balsamic acid, Sumbulamic acid.

When Sumbul balsam is distilled with water, it affords some essential oil. When distilled alone, a yellowish oil first passes over, and then a greenish one; but on raising the temperature, the whole retort fills with blue vapours, and a dark blue oil passes over. The yellow oil distils over below 212°, the green oil at 212°, and passes over readily with aqueous vapour. The green oil resembles cajuput oil, has a burning taste, an agreeable and peculiar odour, is very volatile and inflammable, and affords with alcohol a solution which is turned red by sulphuric acid. The blue oil does not pass over with water, but becomes, during the boiling with water, bluish-green. It is coloured brownish-green by sulphuric acid, and a bright green oil is separated; it dissolves in alcohol with a blue colour, and the solution rubbed on to paper acquires, after a few days' exposure to the atmosphere, the odour of musk; it is scarcely attacked by cold solution of caustic potash, but is coloured olive-green; it is gradually dissolved by boiling caustic potash.—*Jahrb. d. Prakt. Pharm.*, vii. p. 79.

Analysis of Radix Bryoniæ. *By* M. Schwertfeger.

Bryony root, gathered in spring, contains in 1000 parts—

Water	843·0
Woody fibre	21·3
Albumen	31·2
Starch	41·2
Amorphous bitter substance	19·0
Crystalline bitter substance	2·6
Resin	8·75
Gum	12·0
Sugar	7·5
Malate of potash	0·61
Malate of lime	0·32
Phosphate of lime	0·21
Phosphate of magnesia	0·12
Silicate of alumina	0·22
Silica	0·12

The root dug up in summer differs only from its containing considerably less starch and less crystalline bitter substance. The resins offer nothing peculiar; the one is precipitated by basic ace-

ate of lead, the other not; both are soluble in æther and in alcohol, both are of a light brown colour, and possess a very similar taste to jalap resin. The amorphous bitter substance forms a reddish-brown, very bitter extract, insoluble in æther, but soluble in alcohol and in water, and the aqueous solution of which is not precipitated by corrosive sublimate, chloride of tin or tincture of galls. The crystalline bitter substance constitutes nacreous grayish-white needles, united in fasciculi, of a very pungent smell but have no taste; they disengage ammonia on combustion, dissolve in water, alcohol and dilute acids, are insoluble in æther, and are precipitated from the acid solutions by ammonia.—*Jahrb. für Prakt. Pharm.*, ii. p. 287.

CHEMICAL PREPARATIONS.

Preparation of the Perchloride of Iron. By M. Gobley.

Sesquichloride or perchloride of iron exists in the anhydrous state and in the state of hydrate.

To obtain the anhydrous perchloride there are two processes. The first consists in placing in a luted glass or porcelain tube iron hammerings, and inserting the tube in a furnace; the tube should project some distance beyond the furnace. When the apparatus is thus arranged, that portion of the tube where the iron is placed is heated to a temperature below red heat, about 752°, and a current of dry chlorine is then passed through by one of its extremities. The gas is rapidly absorbed, the iron becomes incandescent, and gives off abundant vapours of sesquichloride, which condense in the cold portion of the tube projecting beyond the furnace, in the form of laminæ of a dark violet colour, and possessed of a metallic lustre.

The second process consists in saturating commercial muriatic acid with dry or moist hydrate of the peroxide of iron. The solution is first effected at the ordinary temperature, then assisted by a gentle heat; and when the acid no longer takes up any oxide, the liquid is filtered, evaporated to dryness in a porcelain capsule, taking care to moderate the heat and to stir constantly. The product of this operation is transferred into an earthen retort, and heat gradually applied, taking care not to place any fire near the dome of the retort. Aqueous vapours are first disengaged; when they have ceased a cork is adapted loosely to the aperture of the retort, and the fire is then raised, so that the bottom of the retort is nearly red-hot towards the close of the operation. The anhydrous perchloride sublimes on to the dome, and into the neck of the retort; when this has cooled sufficiently, it is broken, the chloride removed and transferred immediately into the bottles destined to receive it.

Although the last of the two processes described is the best and most easy of execution, there are many pharmaceutists who are prevented from following it, and the medicinal perchloride of iron of the Codex is that which is obtained by the moist way. Several pro-

cesses have been proposed for the preparation of the hydrated perchloride of iron. The Codex prescribes dissolving red oxide of iron in hydrochloric acid, and evaporating the solution to dryness over the water-bath. This process is bad, for the product always contains, however carefully the evaporation may have been made, a large proportion of insoluble oxychloride.

Thénard, Berzelius and Orfila advise, in their works, dissolving sesquioxide of iron in hydrochloric acid, evaporating the solution to a syrupy consistence, and allowing to cool. The perchloride is deposited in the form of beautiful red crystals, which deliquesce with the greatest facility.

M. Béral proposed preparing it by dissolving precipitated sesquioxide of iron in hydrochloric acid, first cold and then over a water-bath; the solution is transferred into a porcelain capsule, and evaporated at a gentle heat to a syrupy consistence; when arrived at this point, the capsule containing the perchloride of iron is placed by the side of another containing caustic potash or lime, and the whole covered with a bell-glass. The alkali absorbs both the water and the hydrochloric acid, so that in ten to fifteen days the chloride forms a dry, confusedly-crystallized mass, which is then transferred into a bottle under the bell-glass, to prevent the salts deliquescing in the air. This process succeeds very well, but it requires much time, and gives a chloride which is not of constant composition, because it retains variable quantities of water, owing to the method of its preparation.

M. Mohr has recently proposed for preparing perchloride of iron, dissolving hæmatite by digestion in commercial hydrochloric acid, and boiling towards the end of the operation. The liquid is allowed to clarify, is then evaporated to the consistence of a liquid syrup, and placed, well covered, in a cold situation, for instance in a cellar, where it begins to crystallize after some days, and continues to do so for some weeks; the mother-water is decanted and the crystals preserved. M. Mohr analysed the crystals prepared in this manner, and found them to contain 12 atoms of water; he has consequently assigned to it the formula $Fe^2 Cl^3 + 12HO$.

M. Fritzsche, who undertook a fresh investigation in order to determine the proportion of water contained in the chloride of M. Mohr, found that this chloride gave very different results on analysis with respect to the quantity of water, which is equally the case with those obtained by the process described by Orfila, Thénard and Berzelius, and that it was impossible to decide whether it contained 10, 11 or 12 atoms of water; with 10 atoms it should contain 35·92 per cent., with 11, 38·15, and with 12, 40·22. According to the same chemist, on leaving the preceding chloride under a bell-glass with sulphuric acid, the crystals are again converted into a thick liquid, which gives rise to other crystals, containing from 21 to 23 per cent. water; 5 atoms would require 21·9 per cent. According to M. Fritzsche, the same crystals are obtained by fusing the chloride with 10, 11 or 12 atoms of water, and evaporating until a drop solidifies on cooling, and then adding a few drops of concentrated hydrochloric acid before placing it aside to cool.

M. Fritzsche has been led by his experiments to admit the existence of two hydrates of the perchloride of iron perfectly crystalline, between which there is no other crystalline combination.

It will be seen from the above that the processes which have been described for the preparation of the hydrated perchloride of iron are very numerous; but it may be said that neither admits of the perchloride being obtained of a constant composition, in a short time, entirely soluble and capable of long preservation. The principal cause of the easy alteration of the chloride of iron prepared by the processes described, appears to be the large quantity of water which the preparation retains; for instance, that of M. Béral, which contains least, affords, shortly after its preparation, a perceptible deposit of oxychloride when dissolved in water.

Induced by M. Soubeiran to find out a practical process which would allow of obtaining in a short time a perchloride of iron completely soluble, and of a constant composition, I believe I have succeeded by submitting the solution of sesquioxide of iron in hydrochloric acid to the two following conditions of evaporation:—1st, evaporation at a temperature not exceeding 212°, and 2nd, evaporation in perfectly dry air.

After several experiments I stopped at the following process:—Pulverized hæmatite is introduced into a stoppered flask, and a quantity of pure concentrated hydrochloric acid poured over it; there should be an excess of hæmatite; it is then agitated. The two bodies soon react on each other, forming water and perchloride of iron, with disengagement of heat; when the first action is passed over, the flask is placed near the fire and shaken frequently; after several hours' contact it is allowed to subside, and is filtered. The filtered liquid is received in a porcelain capsule, which is placed either on some sand heated by steam or on the head of an alembic, taking care to interpose a piece of flannel between the alembic and the capsule, and to maintain this in its position by means of a piece of string. The apparatus should be so arranged that the steam is conveyed by a long tube into a vessel full of cold water; for it is essential to the success of the operation that no aqueous vapour should circulate around the capsule; since when the liquid is evaporated in an atmosphere charged with humidity, it is decomposed when the salt has reached a certain degree of concentration, hydrochloric acid is disengaged, and sesquioxide of iron precipitated. It must be stirred with a glass spatula during the whole time of evaporation, which is continued until the liquid no longer disengages any perceptible vapours of hydrochloric acid and a drop solidifies on cooling. When it has reached this point, the chloride is poured into perfectly dry phials, provided with good corks; but from this chloride becoming very hard, it is difficult to remove it from the phials. To obviate this inconvenience, M. Soubeiran, who had the kindness to repeat the process, advises its being poured on to a slightly-greased plate, which is immediately covered by another plate, and joined to the first by means of a little luting. After four-and-twenty hours the plates are separated, the chloride broken into

pieces, and immediately transferred into well-dried bottles, which corked with great care.

The perchloride of iron, prepared in this manner, possesses a dark yellowish-red colour, no odour, but a very styptic taste. It is excessively and entirely soluble in water; the solution, which is of a beautiful golden yellow, preserves for an indefinite length of time, exposed to the air, without becoming turbid; it is likewise very soluble in alcohol and æther. Exposed to the air, it rapidly absorbs moisture, which at first it solidifies, but subsequently it deliquesces, and it is therefore necessary to keep it in dry and well-closed bottles. This chloride has the great advantage of keeping for a long time without being decomposed, owing without doubt to the small quantity of water it contains; thus the samples which I possess are as good at present as they were eight months ago, immediately after their preparation.

To ascertain the quantity of water which it contains, I took four samples of the chloride, one of which had been prepared by M. Soubeiran and the other three by myself, 1 grm. of each was decomposed by a gentle heat, and the decomposition assisted by adding several times a few drops of nitric acid. That prepared by M. Soubeiran left 0·393, and the three others 0·392, 0·385, 0·380. The mean of these four quantities is 38·75, which represent 26·86 per cent. iron, which require 52·58 chlorine to form sesquichloride. 100 parts of the chloride consist therefore of—

Iron	26·86
Chlorine	52·58
Water	20·56
	100·00

This chloride contains about one-fifth of its weight of water, or somewhat less than 5 atoms, which require 21·9 per cent. It corresponds to the hydrate with 5 atoms of water of M. Fritzsche.

The process which I propose has therefore the great advantage of affording an entirely soluble chloride of a constant composition, and susceptible of long preservation, which hitherto had not been attained.—*Journ. de Pharm.* for April 1844.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

March 18. (Richard Phillips, Esq., Vice-president, in the Chair.) "On the Occurrence of Fluorine in recent as well as in Fossil Bones," by C. Daubeny, M.D., F.R.S., Professor of Chemistry in the University of Oxford.

Dr. Daubeny having observed the presence of a considerable proportion of fluoride of calcium in the native phosphate of lime of Estremadura, as in the crystallized apatite, was led to investigate

the causes of its presence in fossil and recent bones. The former, it is well known, uniformly contain a considerable proportion of that mineral, varying from 1 to 3 per cent. The proportion found in recent bones is much smaller, and when found as it is by some chemical analysts, but not at all by others. Dr. Daubeny finds that animal matter and carbonic acid in the bones interfere with the usual test for hydrofluoric acid, namely, its effect in corroding glass; but by dissolving the bone examined in dilute acid, and afterwards precipitating the phosphate of lime by ammonia, he uniformly found that substance to be accompanied by fluoride of calcium, sufficient in quantity when mixed with oil of vitriol to corrode glass. He satisfied himself also that this effect was not produced from pure phosphate of lime itself, and cannot therefore be ascribed to a corrosive action of volatilized phosphoric acid.

"On Spathic Carbonate of Iron," by John Thomas Way.

After stating the mineralogical characters of this mineral, Mr. Way gives the analysis, and states it to consist of—

Carbonic acid	36·08
Protoxide of iron	50·75
Peroxide of iron	8·93
Lime	4·24
Water	1·08
	101·08

and therefore expresses its composition as—

Carbonate of protoxide of iron	83·60
Carbonate of lime	7·47
Hydrate of peroxide of iron	10·01
	101·08

and points out the peculiarity of the absence of manganese in this mineral, as from all recorded analyses of spathic carbonate of iron, and also of carbonate of iron existing as clay iron stone, manganese is a usual ingredient.

The remarkable purity of this mineral Mr. Way considers as of great importance in the production of the best varieties of steel, which would enable it to rival successfully the Swedish ore, so esteemed for its conversion into iron of the best quality for the manufacture of steel. Mr. Way states that this mineral (originally of a blackish colour), when treated with dilute muriatic or other acids, is only at first partially acted upon, entirely dissolving out the hydrated peroxide of iron and leaving a white crystalline powder; the composition of which Mr. Way states he found from analysis to consist of—

Carbonate of protoxide of iron	91·24
Carbonate of lime	8·97
	100·21

Mr. Way is unable to give the locality of this iron ore; it came from Hull, and forms a vein of from 4 to 10 fathoms in thickness by upwards of 100 fathoms in width, within about 15 miles of coal

and railway. He concludes by recommending that the attention of mineralogists should be drawn to the subject, as it is by no means improbable that similar spathic iron ore may exist in other localities to an equally large extent.

Meeting of the Royal Institution.

Tuesday, March 19, 1844.

Mr. E. Solly delivered a lecture on the chemistry of vegetation, and its application to agriculture. This discourse commenced by a short sketch of the general nature of organic matter, describing the composition of plants, the conditions necessary to their growth, and the sources whence they derive the substances which constitute their food. Mr. Solly pointed out the cause of the exhaustion of soils, and described the various methods adopted to restore fertility, giving a sketch of the principal substances employed as manures, and the principles on which their action depends. After phosphorus, alkalies, &c. were treated of, attention was drawn to sulphur, an element existing in most plants, especially of those which formed the food of animals. Mr. Solly stated from experiments, that sulphuretted hydrogen, so far from being poisonous to plants, was, when in small quantities, conducive to their vigour and luxuriance. Very conclusive experiments were then exhibited to prove that solid substances, in such minute quantities as to evade all chemical tests, were occasionally suspended in the air. Thus the steam arising from a strong boiling solution of carbonate of soda was proved by the yellow colour it conferred on flame to contain a notable quantity of the solid salt. The manner in which fixed substances derive volatility from their combination with volatile substances was illustrated by visible white flocks of phosphoric acid, which had risen in vapour when heated with sal-ammoniac. Mr. Solly then called attention to the enormous extent to which artificial manures are adulterated. He mentioned an instance where an article contained only one thirty-third part of the salt for which it was sold. He proceeded to refer to the experiments which he had made on manures at the Horticultural Gardens, and which are published in the Horticultural Transactions. He dwelt on the probable effects of muriate of lime to increase the retentive power of the soil for moisture, and suggested that this salt might be effectual in hastening the growth of turnips beyond the period at which they are attacked by the fly. Mr. Solly then drew attention to the remarkable fact that the fossil bones of extinct animals contain a considerable quantity of fluoride of calcium; thus the bones of the Colossochelys, or great tortoise, discovered in the Himalaya Mountains by Messrs. Falconer and Cautley, contain 11 per cent. of fluoride of calcium; whilst recent bones, on the other hand, are found to contain little or no fluoride of calcium. It is reasonable to suppose that the earthy matter constituting the bones of these extinct animals was originally derived from plants; and hence the interesting question—Whence comes this fluoride? It might be supposed that the fluoride had passed into the substance

of the bone by some subsequent process. It might be supposed that the plants on which the animals fed contained fluoride of calcium; or lastly, it might possibly be that some nearer relation existed between phosphorus and fluorine than we were yet acquainted with; and it was not impossible that the one might be converted into the other: this was mentioned merely as a curious speculation—possible, though perhaps not probable. In the mean time it was interesting to observe the action of fluoride of calcium in growing plants; and accordingly experiments had been instituted, the result of which, as far as they could be ascertained at this early period, seemed to favour the conclusion that the fluoride was absorbed, and therefore that it might possibly to some extent supply the place of phosphate of lime in plants. Mr. Solly concluded with some general remarks on the progress of agricultural chemistry, and the probable results of its future study; expressing a regret that many are so sanguine as to the immediate benefits to be derived from it, that they can hardly fail to be disappointed by the results, as the latter will inevitably fall short of their expectations.—*Athenæum.*

PATENT.

Patent granted to Alexander Parkes, Birmingham, *for Improvements in preparing Solutions of certain Vegetable and Animal Matters, applicable to preserving Wood and other Substances, and for other Uses.*

This invention consists in preparing solutions of vegetable and animal matters, by the employment of *eupion*, or the bisulphuret or other sulphuret of carbon. The vegetable matters referred to are india-rubber, gum mastic and other gums and resins; and the animal matter is phosphorus.

To form a solution of india-rubber, the patentee adds to each $\frac{1}{2}$ lb. of that substance 2 lbs. of either of the above solvents (preferring the bisulphuret of carbon, on account of its rapid volatilization), which he says will dissolve it without heat quicker than any other solvent hitherto employed; and the solution thus produced is passed through a linen or other strainer, to remove any impurities that may exist in the india-rubber. This solution is now ready for use, either in combination with other substances, such as sulphur, for the purpose of impregnating wood; or alone, as a water-proof coating; it should be kept either in closed vessels, or under water, to preserve its moisture. For some purposes the solution is made by adding $\frac{1}{4}$ lb. of bisulphuret of carbon and 3 lbs. of turpentine or naphtha to each pound of india-rubber.

When a solid mass or block is required, 7 lbs. of the bisulphuret of carbon are added to every 10 lbs. of the india-rubber; and this mixture, after remaining in a close vessel for about two hours, will be soft enough to be kneaded by hand or machinery, and formed into blocks. These blocks may be dried in the open air; but it is

preferred to place the moulds containing them in a stove, heated to from 70° to 105° Fahr., with a refrigerator attached, to collect the bisulphuret of carbon as it passes off. After this drying is effected the blocks may be cut into threads or strands if desired, which will according to the patentee's statement, possess the original elasticity of undissolved india-rubber.

The bisulphuret of carbon, or the other solvent, is also used, as above mentioned, for dissolving gum copal, mastic, amber lac, or other gums and resins, to be employed for preserving wood, manufacturing varnishes, and other uses; and for some purposes a portion of india-rubber in solution may be likewise mixed with the gums or resins. 6 lbs. of the solvent may be used to each pound of gum or resin; but these proportions will vary according to circumstances. The addition of 1 oz. of camphor, or 4 oz. of sulphuric æther, will facilitate the action of the solvent above named.

The solution of phosphorus is prepared by adding to each pound of that substance 15 lbs. of the bisulphuret or other sulphuret of carbon, and then thoroughly agitating the mixture. This solution is applicable to various uses; and, amongst others, the patentee employs it for obtaining deposits of metal upon non-metallic substances, either by combining it with the substance on which it is to be deposited, as in the case of wax, or by coating the surface thereof. Any of the known preparations of wax may be treated in this way, but the one preferred by the patentee is composed of from 6 oz. to 8 oz. of the solution, 5 lbs. of wax, and 5 lbs. of deer's suet, melted together at a low heat, on account of the inflammable nature of the phosphorus. The article formed of this composition is acted upon by a solution of silver or gold, in the manner hereafter described with respect to articles which have been coated with the solution.

If the solution is to be applied to the surface of the article, an addition is made to it of 1 lb. of wax or tallow, 1 pint of spirits of turpentine and 2 oz. of india-rubber, dissolved with 1 lb. of asphalte in bisulphuret of carbon for every pound of phosphorus contained in the solution; the wax or tallow being first melted, the solution of india-rubber and asphalte is stirred in; then the turpentine, and after that the solution of phosphorus is added. The solution prepared in this manner is applied to the surfaces of non-metallic substances, such as wood, flowers, &c., by immersion or brushing; the article is then immersed in a dilute solution of nitrate of silver, chloride of gold or other suitable metallic solution, and in a few minutes the surface is covered with a fine film of metal, sufficient to insure a deposit of any required thickness on the article being connected with any of the electrical apparatus at present employed for coating articles with metal. The solution preferred to be used is prepared by dissolving 4 oz. of silver in nitric acid, and afterwards diluting the same with 12 gallons of water; the gold solution is formed by dissolving 1 oz. of gold in nitro-muriatic acid, and then diluting it with 10 gallons of water.—Sealed June 27, 1843.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Narcotine and the Products of its Decomposition. *By* Prof. Wöhler.

This investigation was undertaken in the hope that the products of decomposition of the vegetable alkaloids, of which as yet very little is known, might throw some light on the peculiar constitution and mode of origin of this remarkable class of bodies. For several reasons narcotine was first selected. Exposed in the presence of an acid to oxidizing influences, it is decomposed into an acid containing no nitrogen, into an organic base and carbonic acid. This decomposition is best effected by heating a solution of narcotine in excess of dilute sulphuric acid, with finely-pulverized hyperoxide of manganese as long as any carbonic acid gas is given off. The new acid has been called opianic acid, the new base cotarnine.

1. *Opianic Acid.*—This was discovered some years ago in conjunction with Prof. Liebig. It subsides, on the cooling of the above mixture, as a yellow mass of minute crystals. It is readily obtained perfectly colourless by treatment with hypochlorite of soda; it crystallizes in thin narrow prisms, which are frequently ramified, arborescent, or united in concentric radiating groups; it has a very faintly bitter taste, is slightly soluble in cold water, but much more soluble in boiling water, so that a hot saturated solution solidifies on cooling to a mass of crystals. It melts at 284° without parting with any water; it is not volatile, but creeps up the sides of the vessel so much that it distils over; it burns with flame; its vapour possesses an aromatic odour, and calls to mind that of heated narcotine.

It undergoes a very remarkable change on being submitted to the influence of heat. The melted acid remains soft and transparent for several hours; it then becomes white and hard, beginning at the surface, but so slowly that a transparent soft nucleus may be found after several days in large fused masses, resembling in this respect arsenious acid. It has now become insoluble in water and alcohol, nay even in dilute alkalies. If water be added to it while it is still clear and amorphous, it becomes milk-white, and on boiling is converted into a white earthy mass, of which extremely little dissolves, and which again separates on cooling in white amorphous flakes. The melted insoluble acid was found on analysis to possess the same

quantitative composition as the crystallized. The explanation of this isomerism will appear subsequently.

The analysis of opianic acid and of its salts of silver and lead afforded for the crystallized acid the formula $C^{20}\,H^{8}\,O^{9} + HO$; in the salts the water is replaced by 1 atom of base. The atomic weight of the anhydrous acid is 2502·23.

Opianic acid forms with barytes, oxide of lead and oxide of silver, readily-soluble salts, which crystallize well and part with water of crystallization by exposure to heat.

2. *Opianic Æther.*—This body could not be obtained by acting with muriatic acid gas on a solution of opianic acid in alcohol, but it is readily obtained by employing sulphurous instead of muriatic acid. It crystallizes on evaporation of the concentrated solution in minute colourless prisms, united into bundles and spheres. It possesses no odour and scarcely any taste; it is insoluble in cold water; when heated with it, it melts at about 212° to a clear heavy liquid, which on cooling solidifies to a white radiately-crystalline mass, with considerable contraction; it sublimes. Boiled for some length of time in water, it gradually dissolves, being converted into alcohol and opianic acid; this is very rapidly effected by caustic potash. The analysis confirmed its being opianate of the oxide of æthyle $= C^{4}\,H^{5}\,O + C^{20}\,H^{8}\,O^{9}$.

3. *Opiammon.*—This is a product of the metamorphosis of the opianate of ammonia; it forms on the evaporation of a solution of this salt. The conversion is completely effected on heating the dried saline mass cautiously and equally to somewhat above 212° as long as ammonia is given off. At last it is converted into a pale lemon-yellow powder, which is opiammon. In its perfectly pure state it is probably colourless; it appears crystalline under the microscope. It is entirely insoluble in water, but when heated with water to 302°, it forms a clear solution, and on cooling opianic acid crystallizes from a solution of opianate of ammonia. Opiammon melts readily and creeps up the sides of the vessel, but is not volatile. It is not altered by dilute hot acids.

From the results of analysis its composition may be expressed by the empirical formula $C^{40}\,H^{17}\,N\,O^{16}$. It originates therefore by the separation of 4 atoms of water and 1 equiv. of ammonia from 2 atoms of opianate of ammonia.

4. *Xanthopenic Acid.*—This is a nitrogenous acid, which is formed by the action of alkalies on opiammon; it is characterized by the yellow colour of its salts. A solution of caustic potash does not at first act upon the opiammon, but it soon begins to dissolve, with a uranium-yellow colour and with contemporaneous disengagement of ammonia. On boiling till this has ceased, a yellow solution is obtained of xanthopenate and opianate of potash. The xanthopenic acid is precipitated by muriatic acid in yellow flakes, and can be filtered before the opianic acid has time to crystallize from the hot liquid. In this reaction three-fourths of the nitrogen of the opiammon are expelled. Xanthopenic acid is a lemon-yellow crystalline powder; it melts and dissolves in alkalies with a uranium-

yellow colour. Heated with soda-lime it disengages ammonia. Its composition has not yet been ascertained.

5. *Opianosulphurous Acid.*—This compound is formed by the action of sulphurous acid on opianic acid; the latter is dissolved in large quantities by the hot aqueous solution of sulphurous acid, without separating on cooling. The solution has a very peculiar bitter taste, and leaves behind for a long time a peculiar sweetish after-taste. Carbonate of lead and barytes dissolve in the liquid, and form beautiful crystalline salts, characterized by their lustre. It reduces selenium from selenious acid, and gold from perchloride of gold.

When the solution of opianic acid in sulphurous acid is evaporated at a gentle heat, the new compound is left as a crystalline transparent mass. It is perfectly free from smell. When treated with water it becomes milk-white, and acquires a strong odour of sulphurous acid. The separated white substance is unaltered opianic acid; this decomposition however is only partial.

The analyses of the lead and barytes salts have shown that the composition of this body may be expressed by the formula $C^{20}\ H^{6}\ O^{7}\ 2SO^{2} + HO$. The atom of water represents the bases in the salts. The author will subsequently return to the consideration of its peculiar composition.

6. *Sulphopianic Acid.*—This is an organic compound with sulphur, which is generated by the action of sulphuretted hydrogen gas on opianic acid, dissolved in water at a temperature of 158°. A gradually increasing turbidness results, which appears like precipitated sulphur; the body however which separates, and into which the whole of the opianic acid is converted, is the new compound. The gas must be passed through several days before the action is complete. The sulphopianic acid separates as a yellowish powder. On heating the liquid to boiling, the precipitate melts to a pale yellow clear oil, which sinks to the bottom and solidifies on cooling.

In this state the sulphopianic forms an amorphous, transparent, sulphur-yellow mass; below 212° it becomes soft, and at that temperature entirely liquid; heated more strongly, it is decomposed, giving off voluminous sulphur-yellow vapours, which condense into minute yellow acicular crystals, which are readily soluble in alcohol. It burns with flame and with the odour of sulphurous acid. It is entirely soluble in alcohol, with a yellow colour; if it had been melted, it is again obtained, even on spontaneous evaporation, in an amorphous state; but if the temperature had been so arranged at its formation that the precipitate could not become soft, it separates from the alcohol in minute yellow prisms; it undergoes therefore a similar metamorphosis at its melting point as the opianic acid. It is dissolved by alkalies with a yellow colour, from which it is precipitated by acids in the form of a yellow emulsion, and without any disengagement of sulphuretted hydrogen. After some time however these solutions contain an alkaline sulphuret. In their unaltered state they afford with salts of lead and silver brownish-yellow

precipitates, which are converted at a boiling heat into black sulphurets.

Sulphopianic acid is constituted according to the formula $C^{20}H^8O^7S^2$. It may therefore be regarded as hydrated opianic acid, in which 2 atoms of oxygen have been replaced by 2 atoms of sulphur; its formation is therefore quite simple.

The existence and composition of these bodies derived from opianic acid appear to afford some explanation respecting the true nature of this acid. The elements of 2 atoms of water are evidently removed from its composition by the influence of sulphurous acid and sulphuretted hydrogen, equivalent quantities of which take their place. To the author it appears most simple to admit, that besides the atom of water substitutable by bases, these 2 atoms of water are contained likewise as such in the opianic acid in a state of combination, in which they cannot be separated by bases, just as little as the organic body contained in benzoe-sulphuric acid separates from the sulphuric acid on its union with bases. The author regards opianic acid as a conjugated acid, the copula in which consists of 2 atoms of water, which can be replaced by other copulæ, as sulphuretted hydrogen and sulphurous acid. Opiammon must then be considered as belonging to this series; it is a conjugated combination of 2 atoms of opianic acid, $2 \times (C^{20}H^6O^7)$, with 1 equiv. ammonia and 2 equiv. water, *i. e.* a combination of 1 atom of opianic acid with water for copula, and 1 atom of opianic acid with ammonia for copula. This view will be rendered intelligible by the following formulæ. The excluded atom of water is that which is replaceable by bases:—

Opianic acid $= HO + (C^{20}H^6O^7 + 2HO)$.
Opianosulphurous acid $= HO + (C^{20}H^6O^7 + 2SO^2)$.
Sulphopianic acid $= HO + (C^{20}H^6O^7 + 2HS)$.
Opiammon $= (C^{20}H^6O^7 + 2HO) + (C^{20}H^6O^7 + NH^3)$.

The latter might also be regarded as biopianate of ammonia $= (NH^4O + C^{20}H^6O^7) + (HO + C^{20}H^6O^7)$. But it certainly is not a salt.

If this latter view is correct, it becomes highly probable that narcotine itself likewise belongs to this series, and is a body of analogous composition to opiammon, in which opianic acid may be admitted as pre-existing in the above sense.

The melted and insoluble opianic acid is probably a totally different body, but isomeric with the crystallized opianic acid, and has probably originated from the opianic acid having assimilated the elements of the 2 atoms of water under the influence of heat. If it consists of two bodies, as the microscopic examination tends to show, these together possess, as the analysis indicates, the composition of the crystallized opianic acid.

[To be continued.]

On Soluble Albumen. By Adolphe Wurz.

Animal albumen almost always occurs in alkaline liquids, which are moreover charged with various salts. It has been supposed that its solubility in water was owing to the presence of these inorganic substances. Such is the opinion advanced by M. Scherer*. However, the experiments on which this opinion is founded are not free from objection, and the conclusions which have been drawn from them will be found to be completely invalidated by the facts which will be detailed in this notice. I have succeeded in removing from albumen the foreign principles which accompany it without altering its solubility in water. The following is the process which I employ for preparing pure albumen :—

White of egg, mixed with twice its volume of water, is passed through linen, in order to tear the cells. A little diacetate of lead is poured into the filtered liquid, which occasions an abundant precipitate. An excess of the lead salt should be avoided, otherwise the precipitate would dissolve in it. After edulcoration the mass is mixed in water so as to form a thin paste, and a current of carbonic acid passed into it.

The liquid, at first thick, soon loses its consistence, and at the same time a considerable froth is formed. The albuminate of lead is decomposed by the carbonic acid, forming carbonate of lead and free albumen, which dissolves in the water. It is filtered through paper, washed with acid in order to separate an albuminous deposit, of which I shall speak subsequently. The albumen which has passed through the filter is not yet pure ; it contains traces of oxide of lead, some drops of sulphuretted hydrogen are poured into it, which renders the liquor brown ; but it remains transparent, for the sulphuret of lead is not precipitated. To separate it, the liquid is heated with care at a temperature of 140° Fahr. until it is rendered turbid ; the first flakes of albumen carry down with them the whole of the sulphuret of lead. The filtered liquid is evaporated in large shallow dishes at a temperature of 122° ; the residue is soluble albumen in a state of purity.

The solution of albumen in pure water and coagulated albumen possess a weak acid reaction. When coagulated albumen is digested at a gentle heat with carbonate or bicarbonate of soda, it combines with the soda, expelling the carbonic acid. If the substance is collected after some time on a filter, and submitted to long-continued washings, it behaves perfectly neutral towards litmus-paper, but on incineration it leaves a strongly-alkaline residue.

M. Hruschauer has likewise observed this acid reaction with albumen precipitated by sulphuric acid and purified by long washing ; on the other hand, Dr. Bence Jones and M. Rochleder have proved that perfectly pure caseine and legumine slightly redden tincture of litmus.

If a solution of pure albumen be heated to 139° it becomes turbid,

* Ann. der Chem. und Pharm., vol. xi. p. 1.

from 142° to 146° flakes form in the liquid, and at a slightly higher temperature the whole solidifies. Solution of pure albumen therefore behaves exactly like white of egg.

I took the greatest care to verify and to ascertain all these properties of pure albumen, in order to confirm its identity with the substance which exists in the white of egg. The analysis of several samples of pure albumen have given the following results:—

	Soluble albumen.		Insoluble albumen.	
			a.	*b.* Treated with æther.
Carbon	52·88	52·70	52·92	52·82
Hydrogen..	7·19	7·06	7·15	7·23
Nitrogen ..	15·55	15·55	15·65	
Oxygen, &c.	24·38	24·69	24·28	

It will be seen that the composition of the albumen, purified by the process above described, is constant; these analyses agree moreover with those which have been published by MM. Dumas and Cahours.

I have likewise endeavoured to purify the albumen from serum, but the precipitate formed by subacetate of lead in serum of the blood is but very imperfectly decomposed by carbonic acid, and only furnishes liquids which contain very little albumen. I have consequently been compelled to give up this mode of purification.—*Comptes Rendus*, April 15, 1844.

Action of Perchloride of Copper upon Sulphuret of Mercury. *By* M. Rammelsberg.

According to M. Karsten, sulphuret of mercury dissolves, without any perceptible alteration, in a concentrated solution of perchloride of copper. When sulphuret of mercury, which has been precipitated by sulphuretted hydrogen from perchloride of mercury and well edulcorated, is digested while still in the moist state with a large quantity of a concentrated solution of chloride of copper, it dissolves, and the solution acquires a brownish tint from the formation of protochloride of copper. The solution however is not complete, for a quantity of sulphur, which on account of the dark colour of the liquid is not immediately perceptible, separates, and coheres to a mass on boiling the solution.

If a larger quantity of sulphuret of mercury be employed, and this gradually conveyed into the hot solution of perchloride of copper, the former is converted into an orange-yellow powder of brilliant colour, which rapidly subsides, and on heating the whole to boiling neither changes its colour nor loses its pulverulent form. It is easily washed, which is continued until the water which passes through is not rendered perceptibly turbid by solution of silver; it may then be dried by exposure to the air without decomposition.

The filtered liquid, which still contains much perchloride of copper, exhibits more of a brown colour, and affords on dilution with water, a white precipitate of protochloride of copper; it contains no

sulphuric acid, but mercury is undoubtedly present, probably as perchloride, in combination with perchloride of copper.

Heated without access of air, the substance becomes black, melts with tumescence, and then again solidifies. In this operation a sublimate forms, at first of sulphur, then of perchloride and sulphuret of mercury, from which the former may be extracted by water. The powder is scarcely acted upon by muriatic acid. Nitric and nitro-muriatic acids dissolve it, with separation of sulphur; on being treated with caustic potash, it is instantly blackened; the alkaline liquid contains, as proved by its behaviour towards acids and salts of silver, chloride of potassium and a considerable quantity of hyposulphite of potash. The black residue yields but little copper and mercury to muriatic acid, but dissolves in nitric acid, with separation of sulphur. The following results were obtained on analysing the precipitate:—

Hyposulphurous acid....	5·01	16·3 sulphur.
Sulphur	13·09	
Chlorine	9·13	
Copper	16·02	16·55
Mercury	57·04	56·58

Notwithstanding the constant composition, the precipitate is evidently a mixture of free sulphur ($1\frac{1}{2}$ atom), of a hyposulphite, probably the double salt $3HgO, SO^2 + 5Cu^2 O, SO^2$, and of a sulphuret and chloride of copper and mercury (either $2(HgCl + HgS) + 3CuS$, or $HgCl, 2HgS + HgCl, 3CuS$).

In the action of sulphuret of mercury upon perchloride of copper, there first originates perchloride of mercury and sulphuret of copper; but a portion of the perchloride of copper is reduced to protochloride, with formation of perchloride of mercury (and probably also of hyposulphite of the peroxide of mercury), and separation of sulphur; while another portion meets with a similar reduction from the sulphuret of copper formed, hyposulphurous acid and protoxide of copper being generated by the action of the water.—Pogg. *Annalen*, lxi. p. 401.

Coating of Copper with Arsenic.

M. Reinsch proposes covering the copper sheathing of vessels with a thin layer of arsenic in the moist way. This coating would cost very little, would not be acted upon by the salt water, and would prevent mollusca from adhering to the bottom and sides of the vessel as effectually as verdigris.—*Jahrb. für Prakt. Pharm.*, vii. p. 94.

On the Preparation and Composition of Saccharic Acid, and on some of its Salts. *By* M. Heintz.

The composition of this acid has hitherto remained doubtful, inasmuch as the most recent investigations, those of Hess and Thaulow, are far from agreeing with each other. At the wish of Prof. Rose, M. Heintz has instituted fresh experiments on the subject,

with the following results. M. Heintz employed a far more advantageous method for the preparation of this acid than that adopted by former chemists. In the preparation of saccharic acid by the action of nitric acid on cane-sugar, the chief object is to avoid as much as possible the formation of oxalic acid. This it has been sought to attain by diluting the nitric acid with water, but without success; it is however effected by avoiding too high a temperature. If 3 parts nitric acid, of spec. grav. 1·25 to 1·30, are allowed to act on 1 part sugar at 122°, only traces of oxalic acid are formed, and sometimes scarcely any.

With this acid the sparingly-soluble bisaccharate of potash should be immediately prepared, by saturating with carbonate of potash, and adding so much acetic acid that the mass smells faintly of it. This acid decomposes only the neutral but not the acid salt, as is the case with the tartrate of potash; the latter, from its requiring about 90 parts of cold water for its solution, separates very gradually, for the most part in beautiful crystals; the mother-ley should not be thrown away, as after weeks and months crystals still separate from it. The coloured salt, after having been pressed between blotting-paper, is dissolved in boiling water and purified by recrystallization; it is thus obtained perfectly colourless without the employment of charcoal.

To obtain the acid, the bisaccharate of potash should not be converted into the lead salt, for the saccharate of lead has the peculiarity of combining with the salts of lead employed in its preparation, forming peculiar double salts. The saccharic acid may be isolated by accurately decomposing the saccharate of barytes with sulphuric acid; but since the slightest excess of sulphuric acid blackens the product on evaporation, and it being moreover impossible to separate any undecomposed barytic salt from the acid by means of alcohol, the author prefers decomposing the saccharate of cadmium with sulphuretted hydrogen.

On evaporation in the water-bath to the consistence of a syrup, and complete desiccation in vacuum over sulphuric acid, saccharic acid is obtained as a brittle mass, which immediately absorbs moisture on exposure to the air. The author obtained, according to this method, nearly 6 parts of perfectly pure bisaccharate of potash, or 5 parts of free acid from 100 parts sugar, while formerly only one-third per cent. had been obtained. It does not crystallize, as stated by Guérin Varry and Erdmann; it dissolves readily in water and alcohol, but with difficulty in æther; it is not decomposed by exposure to the air; the concentrated solution does not even become coated with mould, which however is the case with dilute solutions; it is readily converted into oxalic acid by boiling with nitric acid; heated with concentrated sulphuric acid, it is decomposed, gives off sulphurous acid, and becomes black. It is not altered by boiling with a solution of caustic potash, but is decomposed when melted with moist hydrate of potash at about 482° into 1 atom oxalic acid and 1 atom hydrated acetic acid $(6C\,4H\,7O) = (2C\,3O) + (4C\,3H\,4O) + HO$.

The solution of saccharic acid does not precipitate nitrate of silver either in the cold or on boiling; but if the solution be supersaturated with ammonia, the precipitate which at first originates is redissolved, and after some time metallic silver is deposited from the solution. When the solution is boiled, the sides of the glass are coated with a brilliant metallic mirror.

Many of the sparingly-soluble salts of saccharic acid possess the property of subsiding in the cold as flocculent precipitates, but cohere on boiling to a tenacious mass, and by longer boiling become solid.

Neither the acid nor the bisaccharate of potash or of ammonia diffuse on dry distillation the odour of burnt sugar, which readily distinguishes them from tartaric acid and its salts.

The composition of the acid was first determined by Guérin Varry, who found the anhydrous acid to consist of 4C 3H 6O, and called it hydro-oxalic acid, as it might be imagined to consist of oxalic acid and hydrogen. Erdmann subsequently regarded it, according to his researches, to be isomeric with tartaric acid and identical with metatartaric acid. Upon this Hess determined the composition of the bisaccharate of potash to be 12C 9H 15O + KO, and looked upon the dry acid as being composed of 6C 4H 7O, isomeric therefore with mucic acid. According to the more recent researches of Thaulow, the anhydrous acid is composed according to the formula 12C 5H 11O, but he considered it to be pentabasic, from the analysis of the lead salt, the composition of which he found to be 12C 5H 11O + 5PbO. He supposed 5 atoms of water in the hydrated acid, and in the various salts examined by him this water partly replaced by fixed bases, and wholly in the lead salt. Hess denied the accuracy of this composition, and especially that of the lead salt, in which he found a very varying amount of oxide of lead. He conceived that the saccharic acid had undergone some change in the lead salt of M. Thaulow, as he could not succeed in again preparing the bisaccharate of potash with the acid separated by sulphuretted hydrogen.

M. Heintz has not submitted the acid itself to an analysis, from its not being possible to obtain it of constant weight, even after several weeks' standing in vacuum; he has however examined a large number of its salts.

Saccharate of Potash.—The composition of the acid salt, according to two analyses, was found to be 12C 9H 15O + KO; the neutral salt, which is obtained as a white, readily-soluble crystalline crust on saturating the solution of the acid salt accurately with potash, evaporating to a syrup and then placing it aside for several weeks, was composed of 6C 4H 7O + KO.

Saccharate of Soda.—Only a neutral salt could be obtained, which is very deliquescent, and was therefore not submitted to analysis.

Saccharate of Ammonia.—The solution of the neutral salt dries under the air-pump to a gummy mass. When a solution is heated ammonia escapes, and an easily-crystalline, sparingly-soluble acid

salt separates, which on examination proved to be 12C 9H 15O + NH^4 O.

Saccharate of Magnesia was obtained by boiling a solution of bisaccharate of potash with so little magnesia that the liquid still possessed an acid reaction; it then separates as a sparingly-soluble salt, while neutral salt of potash remains in the solution. When it had been perfectly dried at 212°, it exhibited in three analyses the composition 6C 7H 10O + MgO, or 6C 4H 7O + MgO + 3HO.

Saccharate of Barytes is obtained by adding chloride of barium and ammonia to a solution of bisaccharate of potash, or by mixing saccharic acid with barytic water. It is very sparingly soluble and is anhydrous, being composed of 6C 4H 7O + BaO.

Saccharate of Lime is scarcely soluble, and contains 1 atom of water; formula 6C 5H 8O CaO.

Saccharate of the Protoxide of Iron is readily soluble and not crystalline, which is likewise the case with the *saccharate of the Peroxide of Iron.*

Saccharate of Zinc.—When neutral saccharate of potash is precipitated boiling with sulphate of zinc, the very sparingly-soluble salt boiled with much water, and the filtered liquid allowed to cool, crystals several lines in size may be obtained by frequent repetition of this operation, which on examination exhibited the composition 6C 5H 8O + ZnO, and contained therefore 1 atom water. But if the salt is prepared by dissolving metallic zinc in the acid, a white granular salt is obtained, which is nearly insoluble in water but soluble in saccharic acid, and which has a very remarkable composition. It was found in several analyses to consist of 12C 9H 15O + 2ZnO, or of 6C 4H 7O + ZnO + $\frac{1}{2}$HO, analogous therefore to the composition of the neutral tartrate of potash, according to the researches of Dumas and Schaffgotsch.

Saccharate of Cadmium is almost insoluble in cold and sparingly soluble in hot water. It is anhydrous; formula 6C 4H 7O + CdO.

Saccharate of Lead.—The examination of this salt has led to very interesting results. When saccharic acid is boiled with oxide of lead, the acid combined with this oxide corresponds accurately to the formula 6C 4H 7O, but it is extremely difficult to obtain a perfectly neutral salt. The analyses indicated a small excess of oxide of lead, but they proved it to be an anhydrous salt. When however the salt is prepared by boiling a solution of bisaccharate of potash with acetate, but especially with basic acetate of lead, it contains, even when it has been washed with water from which the air has been expelled, and dried under the air-pump, traces of carbonic acid. The analyses moreover furnished results which did not agree well with one another. This led the author to suspect that the salt might contain acetic acid; and in effect, on decomposing it with sulphuretted hydrogen, and exposing the acid separated from the sulphuret of lead, loosely covered, to the atmosphere until the smell of sulphuretted hydrogen had disappeared, the odour of acetic acid became distinctly perceptible, and when separated by distillation exhibited very distinctly the characteristic colouring of a solution

of peroxide of iron after saturation with a base. Some acetate of the protoxide of mercury, which is a very sparingly-soluble salt, was also obtained from it with protonitrate of mercury. The residue of the distillation afforded, on saturation with carbonate of potash and addition of acetic acid, very distinct crystals of the bisaccharate of potash. The saccharic acid therefore had not been changed in its composition by acetic acid, as suspected by Hess; but the most contradictory results may be explained, if we suppose that the saccharate of lead contained varying quantities of acetate and of carbonate of lead.

M. Heintz has not sufficiently repeated his experiments to decide with certainty whether there exists a double salt of saccharate and acetate of lead in simple definite proportions; but he prepared a crystalline salt by boiling solutions of nitrate of lead with saccharate of potash, which exhibited in several analyses the constant composition $(6C\,8H\,7O + PbO) + NO^5\,PbO$.

It is almost insoluble in water, and can therefore be readily washed. It explodes previous to ignition with a faint light, and becomes black from separated carbon. The nitric acid is readily detected in the salt by the usual method, with sulphuric acid and green vitriol.

Saccharate of Bismuth is obtained when a dilute solution of nitrate of bismuth is precipitated with neutral saccharate of potash; the salt is insoluble in cold, and even in boiling water; it dissolves in acids, but not readily. The author could never obtain this salt of uniform composition; one sample, which exhibited the simplest composition, corresponded to the formula $6C\,4H\,7O + Bi^2\,O^3$; it was therefore a basic salt.

Saccharate of Silver.—The existence of this salt is denied by most chemists who have examined saccharic acid; however, on mixing an excess of neutral saccharate of potash with a concentrated solution of nitrate of silver, a white precipitate is obtained, which remains white on boiling, and becomes crystalline; it is, as was to be expected, anhydrous, and consists of $6C\,4H\,7O + AgO$.

The author endeavoured in vain to prepare a saccharate of the oxide of ethyle.

From this investigation it results that the proportion of the carbon to the hydrogen in most of the salts of saccharic acid is as 6 atoms to 8; in no one, not even in the silver salt, is the amount of hydrogen smaller, but it is larger in several, for instance in those of magnesia, lime and oxide of zinc.

Since moreover saccharic acid forms acid salts with potash and ammonia just like tartaric acid, the question arises whether its atoms should not be doubled, and the acid be regarded as bibasic, or whether those salts should be considered as combinations of neutral salt with the hydrate of saccharic acid. The composition of the double salt of saccharate and nitrate of lead, and the vain attempts to prepare salts of saccharic acid with two strong bases, favour the latter view; M. Heintz accordingly adopts the formula $6C\,4H\,7O$ for the composition of anhydrous saccharic acid. The water in the salts of

magnesia, of lime and of zinc, must be looked upon as water of crystallization; it cannot be expelled from them at 212°, but the saccharate of magnesia parts with it at a temperature of from 302° to 320°, and the amount of magnesia then corresponds to that of an anhydrous salt, and when the salt is treated with water it disengages a considerable amount of heat from its recombining with water. The magnesia could not be separated by potash, and it was found impossible to prepare the bisaccharate of potash by the addition of acetic acid; but the author had already found that small quantities of lime and other bases prevent the formation of the bisaccharate of potash. When however the acid of the heated magnesia salt is combined with lead, an acid can be separated from the so-obtained saccharate of lead by sulphuretted hydrogen, which possesses all the properties of saccharic acid, so that it may be admitted with certainty that the composition of the saccharic acid has undergone no alteration in the strongly-heated anhydrous salt of magnesia.—*Proc. Royal Acad. Berlin*, Jan. 8, 1844.

On the Protocyanide of Potassium and Gold, and on the Protocyanide of Gold. *By* M. Jewreinoff.

M. Himly, in his analysis of these compounds*, has determined the amount of cyanogen by the loss; this circumstance, together with that of the cyanide of gold and potassium being deposited in white crystals from a concentrated solution of gold prepared with cyanide of potassium for galvanic gilding, induced the author to repeat the examination.

The protocyanide of potassium and gold is not in the least affected by exposure to the air or to light, not even to the direct light of the sun; on being heated it parts with no water; on ignition it decrepitates, then melts, gives off cyanogen and gold, is reduced, but the reduction is not complete; for on treating the ignited mass with water, only 11·44 per cent. gold is obtained, and the solution still contains gold. Muriatic acid decomposes the solution of the protocyanide of potassium and gold very slowly in the cold, but rapidly on boiling, disengaging prussic acid, while a lemon-yellow precipitate of cyanide of gold, insoluble in water, nitric and muriatic acids, subsides, and chloride of potassium remains in the solution; the salt however is not entirely decomposed even in this way, for a small separation of gold resulted on evaporation of the filtered liquid and ignition of the residue. This method however may be employed in analysis if the filtered cyanide of gold is decomposed by ignition, the residue weighed, the filtered solution reduced to dryness, the residue fused in a platinum crucible, weighed, then dissolved in water, and the weight of the gold remaining undissolved determined.

The salt may be treated with strong sulphuric acid, when it is decomposed with evolution of prussic acid; the whole is then eva-

* See this Journal, vol. i. p. 239; and for the observations of Messrs. Glassford and Napier, and Mr. J. Carty on these combinations, p. 196 of the present volume.

porated to dryness, the residue ignited for some time, weighed, the sulphate of potash then extracted with water, and the weight of the residue of gold determined. The following are the results obtained in this way:—

	With hydrochloric acid.	With sulphuric acid.		Equiv.	Calculated.
Gold.....	67·69	68·002	68·20	1	68·37
Potassium..	13·18	13·740	13·70	1	13·49
Cyanogen..				2	18·14

These analyses were checked by an analysis of the protocyanide of gold. The lemon-yellow precipitate obtained on decomposing the double salt with hydrochloric acid, left on ignition 88·13, 88·22, 88·21 per cent. of chemically pure gold. On determining the amount of nitrogen according to the method of Varrentrapp and Will, and calculating the amount of cyanogen from the ammonio-chloride of platinum, 11·26 and 11·4 per cent. were obtained. These numbers agree well with the formula, AuCy, for the protocyanide of gold, which requires 88·32 per cent. gold and 11·61 per cent. cyanogen. In the protocyanide of potassium and gold, the cyanogen is equally divided between the potassium and gold, and entirely confirms the formula advanced by M. Himly.

The protocyanide of potassium and gold is obtained of precisely the same composition whether the gold solution has been prepared with oxide of gold, caustic potash and cyanide of potassium, or from chloride of gold, caustic potash and cyanide of potassium; in both cases hydrochloric acid immediately precipitates the lemon-coloured protocyanide of gold. The presence of chloride of potassium is quite indifferent in gilding, as it depends solely on the presence of the above-described double salt, which is far more soluble in hot water than in cold.

The lemon-coloured protocyanide of gold is not affected by nitric, muriatic, or by nitro-muriatic acid, even on boiling; but it is coloured green by caustic and carbonate alkalies and by sulphuric acid; muriatic acid restores the yellow colour.—*Bullet. de l'Acad. de Pétersburg*, ii. p. 289.

PHARMACOLOGY.

On some new Drugs and their Chemical Constituents.
By Dr. L. F. Bley.

[Continued from p. 218.]

II. *Cachalagua.*

This is said to purify the blood. Dr. Martius states "that it is derived from *Erythræa chilensis*. Févillée has figured it, and has given some notices respecting its origin and use. In its bitter taste it greatly resembles our *Centaurea*; it is employed as a stomachic, and also against fever." Geiger gives the following notice:—"*Chironea chilensis*, Willd., Chilian *Chironea Cachalagua*, a plant which grows in Chili, resembling the *Centaurea Centaurium*, with

rose-coloured petals, which are somewhat suberose at the apex." It is administered under the name of Cachalagua in South America as a stomachic and febrifuge. Persoon characterizes it as follows:—

Erythræa chilensis, Willd.; *Centaurea peruviana*, Lam.; Foliis lanceolatis caul. dichotomo corymboso; habitat in regno Chili et Peruviæ.

It has no peculiar odour, but a very bitter taste.

Treatment with Water.—5 drms. boiled with 15 oz. of water down to a third, gave a saturated brown-red decoction, of a strong and persistent bitter taste. The decoction reddened blue litmus-paper, rendered salts of silver turbid, and likewise salts of barytes, but in a less degree; it produced with oxalate of ammonia a considerable turbidness, with nitrate of lead a precipitate, with protochloride of gold a considerable blue turbidness with reduction of the gold, with perchloride of iron a green colour, with tincture of galls turbidness, with solution of gelatine a precipitate, with tincture of iodine a violet-blue colour. Nearly 50 grs. of dry extract were obtained from the above quantity on evaporation; it had a bitter taste, somewhat resembling aloes. Alcohol removed from this extract a bitter resin of a dark brown colour.

Treatment with Alcohol.—The residue, which had been exhausted with water, was now treated with alcohol of 0·863 spec. grav., which removed 9 grs. of an extract, which appeared partly of a light brown partly of a green colour. The taste was resinous and very bitter. It melted in the flame with a fatty odour, burnt with slight tumescence, leaving behind a small quantity of carbon. Water removed from it a small quantity of a bitter substance, amounting not quite to a fourth part; a brown resin and chlorophylle of a bright green colour were left behind. The plant therefore contains gum, starch (which amounted to 3 grs.), a brown bitter resin, chlorophylle, traces of tannine, and some salts. Æther extracted from the residue more chlorophylle; what then remained was void of taste. The small quantity of material at my disposal did not allow of my making further experiments; but from the above, this Chilian plant appears to agree very closely in its chemical constitution with the common Centaury.

III. and IV. *Cascara de Lingue* and *de Pingue.*

These substances are said to contain, according to communications from Mexico, very much tannine, and are stated to produce the same effect in six weeks as oak-bark in a year.

Both substances were unknown to Professor Martius. The latter appeared to him to bear great resemblance to the root of a species of *Curcuma*, and to belong therefore to the *Scitamineæ*.

Physical Description of the Cascara de Lingue.—This bark occurs in fragments of one to three inches in length, and a quarter to an inch in breadth, and from two to three lines in thickness; it is partially provided with an epidermis, upon which at some spots whitish-green lichens occur. The colour of the bark on its outer surface is grayish-brown; the lichens however render it whitish-gray. The outer bark is unequal and full of fissures. The upper

cortical layer is about the thickness of writing-paper; beneath it is a reddish-brown membrane of about half the thickness, which is here and there provided with warty prominences. The true bark is situated beneath these; it is of the colour and appearance of *Cinchona regia*, and like this is but slightly tubular, with a rough fracture. Its odour resembles in some degree the true barks, but its taste is astringent, somewhat mucous, but not at all bitter. The powder resembles that of the *Cinchona regia*; when ignited it gives off vapours which slightly irritate the eyes, leaves behind a somewhat shining coal, and finally a delicate white ash (amounting to about 6 per cent. of the bark), which has a faintly-alkaline taste, and was found on examination to consist of chloride of potassium, sulphate of lime, traces of carbonate of magnesia and carbonate of potash.

Treatment with Water.—1 oz. of the coarsely-powdered bark was boiled with 12 oz. of distilled water down to 4. The decoction possessed a wine-red colour, no odour, but a very astringent taste. It reddened blue litmus-paper slightly, gave a white precipitate with nitrate of silver, was scarcely rendered turbid by a solution of a salt of barytes, became opake with oxalate of potash, gave a considerable precipitate with perchloride of mercury, and also with nitrate of lead; chloride of gold produced a dark bluish-black colour, perchloride of iron a blackish-blue precipitate, solution of isinglass a very considerable bluish precipitate, tincture of iodine a violet-blue precipitate, tincture of galls no opacity. The decoction afforded on evaporation a brownish extract, which was partly redissolved by alcohol, and which left behind on evaporation a small quantity of a pale brown resin, of a somewhat irritating, slightly astringent taste. The portion not dissolved by the alcohol consisted of tannine and gum, with traces of salts and starch, of which 1 oz. of bark afforded 28 grs. The gum and tannine were separated by means of aqueous alcohol, which left the gum undissolved; this was then shaken with cold water, in which it dissolved, while starch remained in part behind, or subsequently separated from the dilute solution. The quantity of tannine amounted approximatively to 55·0 grs.

Another experiment was made to determine the tannine; 1 oz. of the bark was exhausted by boiling with distilled water, the liquid evaporated to 4 oz., the decoction strained quickly through dry paper, and solution of acetate of iron added to it as long as it afforded a precipitate. This was then collected on a filter which had been weighed, the precipitate edulcorated with acidulated water, dried with the filter and weighed; 108 grs. of tannate of iron were obtained.

For the sake of comparison, similar quantities of gall-apples, oak-bark and Rhatanhy root were submitted to the same process. The oak-bark gave 98 grs. of tannate of iron, the galls 251·0 grs., the Rhatanhy bark 104·5 grs. But according to experiment, 100 parts tannate of iron correspond to 53·67 grs. tannine, so that we can easily judge of the value of the bark for purposes of tanning.

To oak-bark it is as ..... 14·5 : 13
To gall-apples as ..... 14·5 : 33·5
And to the Rhatanhy as ..... 14·5 : 13·75

Treatment with Alcohol.—The residuous bark from the aqueous extract digested with alcohol afforded 9·0 grs. of a reddish-brown extract, of a fatty, astringent, and at the same time irritating taste. The extract melted on being heated, burnt with flame, giving off vapours which excited coughing. Water removed from it 4 grs. of an extract containing tannine. The residuous 5 grs. behaved like a soft resin, and possessed a very irritating taste. Æther removed from the residue of the bark a trace of a yellow fatty substance. *Cascara de Lingue* contains therefore tannine, gum, salts, starch, soft resin, vegetable fibre and water.

Physical Characters of Cascara de Pingue.—This substance, which according to Prof. Martius's information is probably the fragments of a root, perhaps of a *Curcuma*, and belongs to the family of the *Scitamineæ*, occurs in fragments of from half an inch to one inch and a quarter in length, a quarter to one inch in breadth, and from four to six lines in thickness, of grayish-yellow colour, inclining in some places to green. At a few places only is the epidermis visible; its colour is greenish-yellow, with here and there black spots. The surface is fissured and warty; fracture uneven, not fibrous. It has no perceptible odour; the taste is somewhat mucous and very astringent; the powder is yellowish-green. When burnt, it smells like fresh-roasted acorns. The ash is white, and possesses a somewhat saline, earthy taste. It contains a little carbonate of magnesia, a little carbonate of lime, much chloride of potassium and sulphate of potash.

Aqueous Extract.—The decoction of the same strength as the preceding exhibited the following properties:—Colour wine-red, but more brownish, no perceptible odour, taste astringent; it turns blue litmus-paper strongly red. Salts of silver give a gray precipitate, salts of barytes a considerable gray precipitate, oxalate of ammonia causes turbidness, lime water a considerable dirty white precipitate, perchloride of iron a greenish-gray precipitate, perchloride of mercury scarcely any turbidness, nitrate of lead a dirty grayish-yellow flocculent precipitate, solution of isinglass considerable precipitate, tincture of galls considerable turbidness, tincture of iodine a pale violet precipitate.

A dark brown extract, of a very highly astringent taste, was obtained from a decoction on evaporation, from which alcohol removed a small quantity of a light brown resin. Gum, tannine, starch (the quantity of which amounted in an ounce of the root to 24 grs.), muriate of lime, chloride of potassium, as well as traces of sulphate of potash, were separated from the aqueous extract. The quantity of the tannate of iron from 1 oz. of the vegetable substance amounted to 153·0 grs.; it is therefore to the *Cascara de Lingue* as 20·52 : 14·5, to oak-bark as 20·52 : 13, to galls as 20·52 : 33·5, to Rhatanhy as 20·52 : 13·75.

Alcoholic Extract.—Exhaustion with alcohol afforded a greenish-brown extract, weighing 140 grs., of a resinous, astringent taste. Held over the flame, it melted, became liquid, burnt with flame, puffing up somewhat. The residuous resin was of a bright yellow colour, of solid consistence, of an acid reaction, and partially soluble in æther. Æther removed from the residuous vegetable matters a small quantity of a yellow matter. The following substances occur therefore, according to these experiments, in the *Cascara de Pingue*:—Tannine, gum, starch, resin, muriate and sulphate of potash and salts of lime, vegetable fibre and water. With respect to the amount of tannine, it even surpasses the *Cascara de Lingue.*—*Archiv der Pharm.* for Feb. 1844.

CHEMICAL PREPARATIONS.

On the Preparation of Pharmaceutical Extracts. By M. Burin.

The method which I propose is founded on the following principles:—

1. A vegetable substance being given, endeavour to ascertain which, among the substances indicated as components by analysis, are those to which the medical action possessed by the substance itself should be attributed.

2. The active principles being known, investigate their chemical properties, in order to ascertain, among other things, what solvents should be employed to separate them as much as possible from those which are inert, and which on that account might prevent the preservation of the product and destroy the energy of its properties.

3. Such a process of evaporation of the liquid parts as will most completely avoid the decomposing action which organic bodies so readily undergo in contact with chemical agents such as heat, air or water.

I will here detail the mode of proceeding based upon these principles, which I have adopted for preparing some extracts, selected from among those which are the most frequently employed:—

Belladonna, Stramonium, Hyoscyamus.

Most of the *Solaneæ*, and the above in particular, contain active principles, the chemical characters of which, and their effects on the animal œconomy, present the greatest resemblance.

To prepare the extracts of Belladonna, Stramonium, Hyoscyamus, and other *Solaneæ*, I take equal parts of leaves and branches at the commencement of the flowering season, and of alcohol of spec. grav. 0·834.

The plant is crushed with care in a marble mortar, expressed with the hands, then again submitted to the action of the pestle; the juice thus obtained is subsequently again mixed with the plant, the alcohol added and left to macerate for six days. The whole is then thrown on a strainer, and the residue submitted to the action

of a powerful press. The combined and filtered liquids are subsequently distilled *in vacuo*, if possible, if not in a water-bath, to remove all the alcohol (by distillation in the water-bath the product undergoes no alteration, as the evaporation takes place beyond the influence of the air). The residue is set aside to cool, and then filtered to separate the chlorophylle which has subsided; it is then evaporated *in vacuo*, or if the necessary apparatus is not at hand, the product is divided into layers of about four-fifths of an inch in thickness, in large tin moulds which have been rubbed with mercury, and left to spontaneous evaporation in a hot chamber, with a constant current of air, at a temperature of 95° to 104°. When the extract has acquired the consistence of honey, it is again dissolved in 3 times its weight of alcohol of 0·834, filtered, distilled over the water-bath to remove two-thirds of the alcohol, and the evaporation completed in the hot chamber.

The product should be preserved in closely-stoppered bottles.

The object of dissolving the spirituous extract in concentrated alcohol is to separate a certain quantity of salts soluble in weak alcohol, and likewise the inert colouring matter of the extract. This process however is not new; it has, in fact, been already employed by M. Dublanc for extract of lettuce, by M. Lombard for extract of aconite; lastly, MM. Georges and Hespe have advised its being employed in preparing aqueous extracts of Hyoscyamus, and other *Solaneæ*, from the dry plant.

The extracts of these three plants, prepared as above described, have a purple yellow colour when spread out in thin layers, and possess the peculiar odour of the plant; they taste at first acrid, the mouth then becomes dry and clammy, with a feeling of constriction of the back of the throat, which is accompanied with an effect on the brain similar to that which is caused by a small quantity of tobacco-smoke to a person unaccustomed to it. They dilate the pupil.

A portion of the extract represents the principles which are soluble in water and in alcohol:—

Of fresh Belladonna	88	parts, or	12	parts of powder.
Of Stramonium	110	...	12	...
Of Hyoscyamus	105	...	16	...

It is composed of yellow extractive, a complex body which retains a certain quantity of the odoriferous volatile oily liquid, and the whole of the crystalline, alkaline substance, or active principle of the plant, in a state of preservation, which should be considered as perfectly normal, all chances of alteration, which might have resulted either from the mode of operation, or the method of evaporation, having been avoided as completely as possible.

Extract of Gentian.

The observations of MM. Planche, Henri and Caventou, and of M. Leconte, have shown the existence of the following substances in gentian:—

A volatile, odoriferous principle, gentisine, caoutchouc, a green oily

substance uncrystallizable sugar, gum, pectic acid, fawn-coloured colouring substance, organic acid and bitter extractive substance.

MM. Henri and Caventou extracted a crystalline substance from gentian, which they considered, under the name of gentianine, to be the bitter principle of the gentian; but this substance, or the gentisine, is, according to MM. Leconte and Trommsdorff, nothing more than a pale yellow colouring substance, which crystallizes in long needles, is insipid and inodorous, and which is mixed in the gentianine with variable proportions of the bitter principle and fatty matter.

From these facts it results that the chemical nature of the bitter substance of the gentian has still to be determined; and it will presently be seen that, as obtained at present, it exhibits the form of an extractive matter, uncrystallizable, and very soluble in alcohol.

Gentian is exhausted by Cadet's process, in three successive treatments, with twice its weight of alcohol of 0·834. The liquids are combined and distilled over the water-bath to remove the whole of the alcohol; the extract obtained is dissolved in distilled water, which takes up the bitter substance, sugar and free acid, and leaves behind the fatty matter combined with gentisine. It is filtered, evaporation completed in a warm chamber, and when the product has been reduced to the consistence of a thick syrup, it is spread in thin layers, by means of a brush, on plates of tin, which have been rubbed with mercury and then slightly wiped over with a piece of linen moistened with a very small quantity of oil of almonds. When the extract is dry, it suffices to knock the back of the tin plate to remove it in beautiful, transparent yellow laminæ, which should be preserved with care in well-stoppered bottles.

This extract contains the aromatic bitter substance, the sugar, free acid, and probably also a certain quantity of gentisine retained by the bitter principle. It represents the active principles of the gentian in a state of great concentration, and may form the basis of excellent preparations.

1 part of the extract is exactly equivalent to 10 parts of the gentian root.

Extract of Digitalis.

As with gentian, three successive digestions in alcohol of 0·834 entirely exhaust the Digitalis of all its bitter and odoriferous constituents; the liquids are mixed, 2 or 3 quarts of distilled water added, or more, according to the quantity of substance under treatment. [The object of adding this water is to divide the chlorophylle, which otherwise carries down with it a considerable quantity of the active principles.] It is then distilled over the water-bath to remove the alcohol, allowed to cool, and filtered to separate the chlorophylle. Treated in the same manner as the gentian, a dry extract is obtained in the form of beautiful transparent laminæ, which are very slightly coloured, and possess in the highest degree the bitter taste and peculiar odour of digitalis; the odour is rendered very perceptible on rubbing the extract, or on moistening it with a little water. There

can be no doubt that this extract is highly energetic and preferable to every other, and that in the hands of a good practitioner it will form the base of preparations of uniform effect.

2½lbs. of pulverized digitalis afforded 108 grms. of dry extract; but taking into consideration the inevitable losses in operating upon larger quantities, it may be admitted that 1 part of extract is equivalent to 10 parts of dry plant.

This extract should not be substituted for the ordinary extracts of digitalis, except when specially ordered.

Extract of Valerian.

Valerian root contains, according to an analysis of M. Trommsdorff,

Volatile oil Resin Peculiar volatile acid (valerianic acid)	Soluble in alcohol.
Aqueous extractive Peculiar substance Starch	Soluble in water.

Experience has shown that the volatile oil, the valerianic acid and the resin are essentially the active principles of the valerian; on the other hand, the aqueous extract is not without action; in this case therefore as much as possible of the first three substances, the solvent for which is concentrated alcohol, should be introduced into the product, and a certain proportion of those which are likewise soluble in water equally admitted.

The following is the process which I advise:—The coarsely-powdered valerian is moistened with twice its weight of alcohol of 0·834 spec. grav. After three days' contact the mixture is conveyed into a displacement apparatus, and treated with an equal weight of alcohol of 0·915 sp. gr.; on distilling the first product over the water-bath, the residue obtained is a mixture composed almost entirely of a dark green resin, holding in solution the entire amount of the volatile oil and of the valerianic acid. This product is placed aside in a well-stoppered bottle, the alcohol obtained by distillation is diluted with distilled water to reduce it to 0·915 spec. garv., and if necessary fresh alcohol of the same specific gravity added sufficient to exhaust the valerian. The liquors are mixed, filtered, the whole of the alcohol removed by distillation, and the residue evaporated in the hot chamber to a pillular consistence; the first product is then incorporated with it, and thus a homogeneous mass obtained, containing in a perfect state all the active parts of the valerian root.

1 part of extract is equivalent to 5 parts of the root.—*Journ. de Pharm.* for May.

Observations on the preceding Article. By M. Soubeiran.

The object to be attained in the preparation of extracts is to concentrate in a small mass the active parts of plants, without at all

altering the state of combination in which they naturally occur. M. Burin proposes to extend the use of concentrated alcohol, already previously recommended, in order to concentrate the active and to remove the inert principles of vegetables. This object seems to be attained with respect to the *Solaneæ*, but is it equally so for the other plants selected by M. Burin? I will here detail two series of experiments, the one relative to valerian, the other to gentian. I operated on the same root in each experiment, so as to have comparative results.

Extract of Valerian.

2¼ lbs. of substance.	Extract obtained.	Relation to the substance.	Water dissolves	Alcohol of 0·921 dissolves	Alcohol of 0·834 dissolves
Process of M. Burin	255 grs.	: 1 :: 4	80 p. c.	80 p. c.	96 p. c.
Process of the Codex.....	205 grs.	: 1 :: 4·83	80 p. c.	94 p. c.	80 p. c.

These two extracts were both very aromatic; that of the Codex however was the least so, and its colour was darker. I diluted them with water, and obtained the following results:—

Extract by M. Burin's process, diluted	800 times,	specific odour destroyed.
... ...	1000 times,	specific taste destroyed.
... ...	2000 times,	bitterness destroyed.
Extract of the Codex, ...	400 times,	specific odour destroyed.
... ...	800 times,	specific taste destroyed.
... ...	1000 times,	bitterness destroyed.

The substitution of alcohol of 0·834 spec. grav. for alcohol of 0·921 does not offer therefore any great advantage.

Extract of Gentian.

2¼ lbs. of substance.	Extract obtained.	Relation to the substance.	Water dissolves	Alcohol of 0·921 dissolves	Alcohol of 0·834 dissolves
Process of M. Burin...	112 grs.	: 1 :: 8·9	the whole, except some flakes.	entirely.	96 p. c.
Process of the Codex	364 grs.	: 1 :: 2·75	98 p. c.	85 p. c.	20 p. c.

Extract by M. Burin's process, diluted	10,000 times,	still very bitter.
... ...	20,000 times,	distinctly bitter.
Extract of the Codex, ...	4,000 times,	decidedly bitter.
... ...	20,000 times,	bitterness destroyed.

The extract with alcohol of 0·834 spec. grav. contains the bitter principle in a state of greater concentration; but what is the cost of this advantage? Three times less product is obtained. Now alcohol of 0·834 is not a very proper vehicle for removing the bitter principles from the root of gentian; when it ceases to act, alcohol of 0·921 takes up a considerable quantity of those active parts; it is therefore undoubtedly preferable for the preparation of extracts.

These two examples suffice to show all the inconveniences which might result from adopting an absolute principle and extending its application. In extracting the soluble substances contained in plants, it should not be forgotten that the solubility peculiar to each of their isolated principles is no longer the same when several are associated, and that we should not judge *à priori* of the action of solvents on each of them.—*Journ. de Pharm. et de Chim.*, May 1844.

Preparation of Butyric Æther.

This æther, which possesses in so remarkable a degree the pleasant odour of apples, is at present very much used as aroma in the manufacture of rum. It is very readily obtained for this purpose, dissolved in alcohol, on saponifying butter with a concentrated solution of caustic potash, dissolving the soap in the smallest requisite quantity of strong alcohol with the assistance of heat, adding a mixture of alcohol and sulphuric acid to this solution until it has a strong acid reaction, and then submitting it to distillation as long as the product has a fruity odour.

The pure æther may be separated from this product by repeated rectification and treatment with chloride of calcium. According to an analysis of M. Borntrager, it appears, prepared in this manner, to consist solely of the æther of butyric acid. The analysis afforded—

		Calculated according to $C^{12} H^6 O$.
Carbon	61·57	62·35
Hydrogen	10·91	10·25
Oxygen	27·52	27·40

Capronic æther contains, according to Lerch, nearly 67 per cent. carbon.—Liebig's *Annalen* for March 1844.

Solution of Caoutchouc.

M. Heusler recommends boiling 4 oz. of caoutchouc with $1\frac{3}{4}$ lb. linseed oil until perfectly dissolved, then passing through a strainer. The caoutchouc is cut into slips, and is well stirred during the boiling with an iron spatula. This varnish is well adapted for rendering shoes, &c. water-tight.—*Jahrb. für Prakt. Pharm.*, vii. p. 369.

REVIEW.

A Practical Treatise on Brewing, based on Chemical and Œconomical Principles, &c. By WILLIAM BLACK, Practical Brewer. Third Edition. Longman and Co.

As brewing is well known to be a chemical art, and as this work professes to supply the brewer with a process based on chemical principles, a few observations on it may very fairly be expected from us; we have perused it with care, but are sadly afraid that the author has over-estimated his capabilities of attaining his object.

And first, as to the drying or curing of malt, on which subject so much has been written of importance to the brewer, and on which Mr. Black says so little.

It is known to all those who study the chemical principles of brewing, that the diastase formed in the barley during its germination is decomposed at a temperature of 212° F., and that malt consequently should never be heated to a temperature approaching this

point in the drying. Dumas (in his 'Traité de Chimie appliquée aux Arts,' vol. vi. p. 450) says that the temperature should never rise higher than 176° to 185° Fahr.

Professor Otto of Brunswick, who was himself a brewer, in his treatise on brewing (in his 'Lehrbuch der rationellen Praxis der Landwirthschaftlichen Gewerbe,' p. 28), says that no roasting of the starch, upon which the colouring of the malt depends, can take place at a temperature of 146° Fahr. Mr. Black contents himself with saying (p. 20), "If a great current of heated air be constantly directed through the malt on the kiln, no danger of acquiring colour need be apprehended," omitting all mention of diastase and its easy decomposition. Now it will be readily understood that air can easily be heated much beyond the temperatures above quoted. Mr. Black recommends the maltster to dry his malt quickly, and without turning it on the kiln; Prof. Otto, a practical brewer and distinguished chemist, to dry it slowly at a gentle heat, turning it often in order to obtain a uniform and pale malt; this is moreover advantageous, he says, as the malt loses much of its pleasant aroma by being heated too highly during the drying. This method agrees very closely with the practice of the Edinburgh brewers, and in these times of "pale ale" we would recommend it to the notice of brewers in this country.

Mr. Black's reason for not turning the malt is a curious one; he says (p. 21), "We know that the portion of the malt nearest the covering of the kiln sometimes feels quite dry, while that on the top is quite damp; if, therefore, by turning we throw this part of the malt upon the top and the wet to the bottom, the steam of the wet malt from below must pass through the drier on the top, thus creating double work; the steam also, by again passing through the drier malt on the top, tends to render it tough." It would be evident, we should imagine, to any one possessed of common sense, that the only way to prevent one portion of the malt becoming drier than the other, is to turn it frequently; nor did we ever meet with a practical maltster who did not agree to this opinion.

The author recommends the practice of redrying malt which has suffered injury by absorbing moisture, and hence acquiring acidity. "Such malts (he says, p. 25), if used without redrying, will invariably produce unsound worts, and consequently bad beer; but if redried previous to mashing, the beer will have a fair chance of being good."

By redrying the evil may no doubt be prevented in a great measure from increasing, but we doubt whether it will be cured; for as the acid formed is lactic acid, which is not decomposed below a temperature of 480°, it is not likely to be got rid of by merely redrying at a temperature of 185°, the highest which can safely be given to it. "Maltsters, therefore, who generally tell you that the redrying of malt spoils it," as Mr. Black remarks, may have some reason for their opinion; for until the malt rises during the process to above 86° Fahr., an additional quantity of lactic acid must be formed in consequence of the elevation of temperature, for according

to MM. Bouton and Fremy the diastase rapidly converts the sugar of malt into lactic acid, when exposed to a temperature of 77° to 86° in contact with air and moisture; and, in fact, we have often procured lactic acid by this method, as being the most convenient and fruitful.

Mr. Black supposes the fermentation of the beer to be very much affected by the electrical conditions of the atmosphere, and recommends all vessels in which beer is to be fermented or stored should be isolated by being placed on supports of baked wood, &c. The reasons he gives for this opinion are by no means satisfactory, nor do his own ideas seem very clear on this point; and a reference to his work will, we imagine, at once produce this conviction. Iron coolers are now becoming very generally used, often of great extent, thus exposing a great surface to the atmosphere, in general connected with the wort in the fermenting tuns by means of copper pipes, &c., circumstances highly favourable for exhibiting the effects of the electrical changes of the atmosphere upon the worts during fermentation. No brewer, however, to whom we had an opportunity of putting the question, has remarked any unfavourable effect that this alteration has had upon his fermentations; nor could we notice the slightest effect produced on a delicate electrometer by a thousand barrels of beer, in an active state of fermentation, contained in a vessel supported on iron pillars, and connected by copper pipes with iron coolers of very great extent.

We must, therefore, in the absence of experiment, which we should have expected in a work based on chemical principles, regard this as a groundless hypothesis. The following paragraph will exhibit the mystification of our author's ideas on this subject (p. 42). "The experiments of Gay-Lussac also clearly prove the important agency of electricity in the process of fermentation. He found that wort to which yeast had been added, when placed in a vacuum, did not undergo fermentation, although all the circumstances were favourable excepting the presence of oxygen. But when an electric spark was passed through the fluid, the fermentation commenced vigorously. The effect here produced, he considered, was by the electric spark decomposing an atom of water, and thus liberating an atom of oxygen, which caused the process to begin. We do not mean to question the high authority of Gay-Lussac, but his experiment does not altogether prove that the particle of oxygen produced was the cause of fermentation. It might perhaps be owing to a more general influence of the electric spark, which in passing through the fluid induced such chemical action of the different component parts upon each other as were sufficient for producing fermentation." As this experiment is not sufficient to convince Mr. Black that the small quantity of oxygen liberated was the cause of the fermentation commencing, perhaps the following one, by the same distinguished philosopher, which Mr. Black may easily repeat on malt wort, may do so, as it does not appear to us to be dependent upon electrical agency at all. This experiment consists in introducing into a tube filled with mercury, and standing in a basin of mercury,

some must or juice of grapes. In consequence of the different densities of the two liquids, the must rises and occupies the upper portion of the interior of the tube; the liquid, thus excluded from the atmosphere, will remain without undergoing any change. But if a small bubble of oxygen gas be introduced, the fermentation speedily commences, if the temperature be not too low, and the vessel becomes filled with carbonic acid, which displaces the mercury.

At page 89 Mr. Black says, "We are now prepared to assert and prove, that when worts are perfectly sound in all the stages of the process, their fermentation will at all times go on regularly and uniformly, if properly managed and with sound yeast. The only difficulty therefore is to know when any such unsoundness has actually taken place. A slight knowledge of chemistry will then not only materially assist us in tracing the evil to its cause, but also enable us, in after-brewings, to prevent its occurrence, should it even proceed from atmospheric influence." [He previously states, p. 88, "that positive electro-chemical action invariably produces acidity, and that negative electricity, although it prevents acidity, retards fermentation."] "As this evil however will sometimes arise, notwithstanding every precaution employed to prevent it, chemistry must be resorted to, to enable us to counteract its baneful effects."

Accordingly we did expect, on reading this passage, that Mr. Black, who pretends to a "*moderate chemical knowledge*," would have favoured us with a little of it; instead of which, however, he informs us how we may ascertain the amount of acidity by *litmus-paper*! as follows (p. 89):—

"If the brewer have a sensitive smell and taste, they will at all times enable him to judge of the soundness or unsoundness of his worts; but when these cannot be depended upon, litmus-paper will be found a very useful substitute. All worts, even when running from the mash-tun, contain a portion of acid, which, *more or less, according to circumstances*, will change the colour of litmus-paper. What we denominate sound worts will give the paper a kind of dirty brownish-red. When we find that the tinge of the paper is a brighter red, there must be additional acid, or perhaps a different acid produced in some part of the process.

"Having *thus* discovered that an excess of acid has been formed, chemistry must be resorted to for discovering the cause; and when found, we shall be enabled to apply the necessary preventives." That is, first catch your hare, and then you may proceed to cook it.

We have no space to extend our remarks on this work. The instructions to private families for brewing their own beer seem judicious, and may be found useful; but small indeed must be the amount of scientific knowledge of any brewer who expects to increase it by a perusal of Mr. Black, whom we would seriously recommend to alter his resolution of not referring to the opinions of others (see preface), in order that he may supply the readers of his next edition with some information that may be more useful to them than vague speculation and gratuitous hypothesis.

PATENT.

Patent granted to Hugh Lee Pattinson, Gateshead, *for Improvements in the Manufacture of White Lead, part of which Improvements are applicable to the Manufacture of Magnesia and its Salts.*

This invention consists in dissolving carbonate of magnesia in water impregnated with carbonic acid gas, by acting upon magnesian limestone, or other earthy substances containing magnesia in a soluble form, or upon rough hydrate of magnesia in the mode hereafter described, and in applying this solution to the manufacture of magnesia and its salts, and to the precipitation of carbonate of lead from any of the soluble salts of lead, but particularly the chloride of lead; in which latter case the carbonate of lead, so precipitated, is triturated with a solution of caustic potash or soda, by which a small quantity of chloride of lead contained in it is converted into hydrated oxide of lead, and the whole rendered similar in composition to the best white lead of commerce. The manner in which these improvements are carried into effect is thus described by the patentee:—I take magnesian limestone, which is well known to be a mixture of carbonate of lime and carbonate of magnesia, in proportions varying at different localities; and on this account I am careful to procure it from places where the stone is rich in magnesia. This I reduce to powder, and sift it through a sieve of forty or fifty apertures to the linear inch. I then heat it red-hot, in an iron retort or reverberatory furnace, for two or three hours, when, the carbonic acid being expelled from the carbonate of magnesia, but not from the carbonate of lime, I withdraw the whole from the retort or furnace, and suffer it to cool. The magnesia contained in the limestone is now soluble in water impregnated with carbonic acid gas, and to dissolve it I proceed as follows:—I am provided with an iron cylinder, lined with lead, which may be of any convenient size, say 4 feet long by $2\frac{1}{2}$ feet in diameter; it is furnished with a safety-valve and an agitator, which latter may be an axis in the centre of the cylinder, with arms reaching nearly to the circumference, all made of iron and covered with lead. The cylinder is placed horizontally, and one extremity of this axis is supported within it by a proper carriage, the other extremity being prolonged, and passing through a stuffing-box at the other end of the cylinder, so that the agitator may be turned round by applying manual or other power to its projecting end. A pipe, leading from a force-pump, is connected with the under side of the cylinder, through which carbonic acid gas may be forced from a gasometer in communication with the pump, and a mercurial gauge is attached, to show at all times the amount of pressure within the cylinder, independently of the safety-valve. Into a cylinder of the size given I introduce from 100 to 120 lbs. of the calcined limestone with a quantity of pure water, nearly filling the cylinder; I then pump in carbonic acid gas, constantly turning the agitator, and forcing in more and more gas, till absorption ceases, under a pressure of five atmospheres. I suffer it

to stand in this condition three or four hours, and then run off the contents of the cylinder into a cistern, and allow it to settle. The clear liquor is now a solution of carbonate of magnesia in water impregnated with carbonic acid gas, or, as I shall hereafter call it, a solution of bicarbonate of magnesia, having a specific gravity of about 1·028, and containing about 1600 grs. of carbonate of magnesia to the imperial gallon.

I consider it the best mode of obtaining a solution of bicarbonate of magnesia from magnesian limestone, to operate upon the limestone after being calcined at a red heat in the way described; but the process may be varied by using in the cylinder the mixed hydrates of lime and magnesia, obtained by completely burning magnesian limestone in a kiln, as commonly practised, and slaking it with water in the usual manner; or, to lessen the expenditure of carbonic acid gas, the mixed hydrates may be exposed to the air a few weeks till the lime has become less caustic by the absorption of carbonic acid from the atmosphere. Or the mixed hydrates may be treated with water, as practised by some manufacturers of Epsom salts, till the lime is wholly or principally removed; after which the residual rough hydrate of magnesia may be acted upon in the cylinder, as described; or hydrate of magnesia may be prepared for solution in the cylinder, by dissolving magnesian limestone in hydrochloric acid, and treating the solution, or a solution of chloride of magnesium, obtained from sea-water by salt-makers in the form of bittern, with its equivalent quantity of hydrate of lime, or of the mixed hydrates of lime and magnesia, obtained by completely burning magnesian limestone, and slaking it as above. When I use this solution of bicarbonate of magnesia for the purpose of preparing magnesia and its salts, I evaporate it to dryness, by which a pure carbonate of magnesia is at once obtained, without the necessity of using a carbonated alkali, as in the old process; and from this I prepare pure magnesia by calcination in the usual manner; or, instead of boiling to dryness, I merely heat the solution for some time to the boiling point, by which the excess of carbonic acid is partly driven off, and pure carbonate of magnesia is precipitated, which may then be collected, and dried in the same way as if precipitated by a carbonated alkali. If I require sulphate of magnesia, I neutralize the solution of bicarbonate of magnesia with sulphuric acid, boil down and crystallize; or I mix the solution with its equivalent quantity of sulphate of iron, dissolved in water, heated to the boiling point, and then suffer the precipitated carbonate of iron to subside; after which I decant the clear solution of sulphate of magnesia, boil down, and crystallize as before. When using this solution of bicarbonate of magnesia for the purpose of preparing carbonate of lead, I make a saturated solution of chloride of lead in water, which, at the temperature of 50° or 60° Fahr., has a specific gravity of about 1·008, and consists of 1 part of chloride of lead dissolved in 126 parts of water. I then mix the two solutions together, when carbonate of lead is immediately precipitated; but in this operation I find it necessary to use certain precautions, otherwise a considerable

quantity of chloride of lead is carried down along with the carbonate. These precautions are, first, to use an excess of the solution of magnesia, and secondly, to mix the two solutions together as rapidly as possible. As to the first, when using a magnesian solution, containing 1600 grs. of carbonate of magnesia per imperial gallon, with a solution of chloride of lead saturated at 55° or 60° Fahr., 1 measure of the former to $8\frac{1}{2}$ of the latter is a proper proportion; in which case there is an excess of carbonate of magnesia employed, amounting to about an eighth of the total quantity contained in the solution. When either one or both the solutions vary in strength, the proportions in which they are to be mixed must be determined by preliminary trials. It is not however necessary to be very exact, provided there is always an excess of carbonate of magnesia amounting to from one-eighth to one-twelfth of the total quantity employed. If the excess is greater than one-eighth no injury will result, except the unnecessary expenditure of the magnesian solution. As to the second precaution, of mixing the two solutions rapidly together, it may be accomplished variously; but I have found it a good method to run them in two streams, properly regulated in quantity, into a small cistern, in which they are to be rapidly blended together by brisk stirring, before passing out, through a hole in the bottom, to a large cistern or tank, where the precipitate finally settles. The precipitate thus obtained is to be collected, washed and dried in the usual manner. It is a carbonate of lead, very nearly pure, and suitable for most purposes; but it always contains a small portion of chloride of lead, seldom less than from 1 to 2 per cent., the presence of which, even in so small a quantity, is somewhat injurious to the colour and body of the white lead. I decompose this chloride, and convert it into a hydrated oxide of lead by grinding the dry precipitate with a solution of caustic alkali, in a mill similar to the ordinary mill used in grinding white lead with oil, adding just so much of the ley as may be required to convert the precipitate into a soft paste. I allow this paste to lie a few days, after which, the chloride of lead being entirely, or almost entirely decomposed, I wash out the alkaline chloride formed by the reaction, and obtain a white lead, similar in composition to the best white lead of commerce. I prepare the caustic alkaline ley by boiling together, in a leaden vessel, for an hour or two, 1 part by weight of dry and recently-slaked lime, 2 parts of crystallized carbonate of soda (which, being cheaper than carbonate of potash, I prefer) and 8 parts of water. The clear and colourless caustic ley, obtained after subsidence, will have a specific gravity of about 1·090, and, when drawn off from the sediment, must be kept in a close vessel for use.—Sealed Sept. 24, 1841.

THE CHEMICAL GAZETTE.

No. XL.—June 15, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Combinations of Gold with Oxygen, with Observations on the Purple of Cassius and Fulminating Gold. By L. FIGUIER.

Protoxide of Gold.—Chemists have described the protoxide of gold as a green powder of great instability, in accordance with the researches of M. Berzelius. These characters do not belong to the protoxide of gold; M. Berzelius did not obtain pure protoxide, but a mixture of metallic gold with this compound.

The protoxide of gold is a violet powder, so dark in the state of hydrate that it appears black; when dried it presents the violet-blue colour of the purple of Cassius. Chemically it is an indifferent compound, which can enter into combination with acids and with bases. Hydracids produce with it a deposit of gold by dissolving the tritoxide formed; ammonia gives with it a violet and fulminating compound. It decomposes at 482° Fahr. Far from presenting the extreme instability which M. Berzelius attributes to it, the protoxide of gold is, on the contrary, the least alterable of all the oxides of this metal.

Hitherto the protoxide of gold had only been obtained by decomposing the protochloride of gold by potash, but it is formed under many other circumstances.

Thus the neutral trichloride of gold, treated with protonitrate of mercury, gives a violet-black precipitate of protoxide of gold. Boiling acetic acid, by reacting on the tritoxide of gold, brings this partially back to the state of protoxide. The acetate, tartrate, and citrate of potash, and the organic acid salts in general, under the influence of a slight excess of free alkali, produce by ebullition a violet-black precipitate of protoxide of gold. Infusions of vegetable or animal matters behave in the same manner. When tritoxide of gold is boiled with caustic potash or soda, a deposit of protoxide of gold is obtained, which goes on increasing according as the ebullition is prolonged. The chloride of gold behaves in the same manner with caustic potash or soda. Lastly, the alkaline carbonates or bicarbonates produce the same reaction with the chloride of gold. The protoxide of gold was easily analysed by the simple action of heat.

Perauric Acid.—I admit the probable existence of an oxygenated

acid of gold, more oxygenated than all the combinations of this kind, soluble in water, or at least in acidulated water, and which will constitute perauric acid, if my researches on this point are confirmed by future experiments. This compound seemed to me to be formed under the following circumstances:—When, as I have already shown, some tritoxide of gold is boiled with caustic potash, there is formed, after rather long ebullition, an abundant precipitate of protoxide of gold. As in this instance no trace of oxygen is disengaged, and as the caustic alkali is absolutely exempt from all organic matter capable of reducing the tritoxide of gold, I think it must be admitted that a more oxygenated combination of gold is formed, which remains dissolved in the alkaline solution. This is in fact observed when the alkali is saturated by nitric or sulphuric acid; the addition of the acid determines the separation of the non-decomposed tritoxide of gold; only carbonic acid is disengaged, and the filtered liquid remains strongly coloured yellow. After a few instants this liquor presents signs of evident decomposition; it quickly turns green, becomes turbid and deposits gold. To observe this phænomenon, it is sufficient to heat it to 140° or 150°, and the deposit of gold is accompanied with extremely small bubbles of gas. This phænomenon may also be observed by employing the ordinary chloride of gold. After having boiled its solution with potash, added long enough to furnish an abundant deposit of protoxide of gold, the liquor is precipitated by some chloride of barium, and afterwards by barytic water. At first a yellow, then a greenish precipitate is formed; this precipitate being treated with sulphuric acid, the tritoxide of gold remains, in an insoluble state, mixed with sulphate of barytes, and the filtered liquor contains the compound in question.

From the preceding facts it seems natural enough to conclude that the tritoxide of gold separates in this instance into protoxide of gold and into a new acid more oxygenated than the tritoxide, and presenting an extreme alterability. This has hitherto prevented me from making a more perfect study of this compound. I shall shortly continue these researches.

Intermediate Oxide of Gold.—Guyton, Oberkampf and Berzelius admit the existence of a purple oxide; M. Berzelius, who examines this question at length in his 'Traité de Chimie,' represents its probable composition by the formula $Au^2 O^3$. Having repeated all the experiments of Guyton, of Oberkampf and of M. Berzelius, I was convinced that in all the reactions quoted by the latter chemist in favour of the existence of his intermediate oxide no oxide of gold is formed; it is always metallic gold which is produced; only in such cases the gold assumes the purple or rosy-purple colour, which it possesses when in its greatest state of division.

Purple of Cassius.—The result of my researches on the purple of Cassius is, that this compound, so often investigated by chemists, is a perfectly definite combination of protoxide of gold and of stannic acid or peroxide of tin. The proof is, that the purple of Cassius is instantly produced when protoxide of gold and peroxide of tin are placed in contact. In order to make the experiment, it suffices to

boil the protoxide of gold with a solution of peroxide of tin in potash for a few minutes. The purple of Cassius is directly formed.

Moreover, reagents show the existence of peroxide of tin in the purple of Cassius, without any trace of protoxide. Thus hydrochloric acid and caustic potash only remove peroxide of tin from the compound; the purple of Cassius and the peroxide of gold possess entirely the same colour.

All chemists who have analysed the purple of Cassius have obtained numbers varying considerably from one another. Analyses of different samples never afforded numbers comparable with each other and corresponding to a simple formula; but having had the notion of submitting these compounds to the action of boiling potash, in order to examine the product, I found that the potash, without altering the primitive composition, removed from it a variable proportion of peroxide of tin, and the purple of Cassius remained with its ordinary properties; in this state it constantly furnished numbers corresponding very exactly to the formula $3(StO^2)\,Au^2\,O + 4HO$. I have been led to this composition by analysing the purple of Cassius formed by means of the protoxide of gold and of the stannate of potash. The purple of Cassius, formed by the curious reaction described by B. Pelletier, and which consists in throwing metallic tin into some chloride of gold, has precisely the same composition.

This formula, which at first seems hardly admissible, enters entirely however into the series of ordinary combinations, as will easily be recognised if it be borne in mind that M. Fremy, in his researches on the metallic acids, showed that 3 equiv. of stannic acid enter into the composition of the neutral salts, so that the formula for the neutral stannates is not (StO^2) but $3(StO^2)\,MO$.

According to this, then, we see that the purple of Cassius is really the neutral stannate of the protoxide of gold. The existence of a corresponding compound, which contains precisely twice as much oxide of tin, and which accordingly represents the bistannate of the protoxide of gold, also confirms the constitution which I assign to the purple of Cassius.

M. Berzelius analysed some purple of Cassius, prepared with solution of tin in nitro-muriatic acid, and found for its composition numbers which, calculated on the supposition of the existence of protoxide of gold, lead to the formula $6(StO^2)\,Au^2\,O + 7HO$.

Tritoxide of Gold.—I shall here mention a new process for the preparation of this compound. It consists in accurately saturating the neutral chloride of gold with carbonate of soda, and boiling until no more precipitate is formed. By this treatment almost the whole of the gold is obtained in the state of oxide. To obtain the rest of the metal in this state, the liquor is supersaturated with carbonate of soda to form aurate of soda, which is neutralized whilst hot by sulphuric acid, when the remainder of the oxide of gold is precipitated. The filtered liquid is almost entirely colourless, indicating that it contains but a very insignificant quantity of gold.

Fulminating Gold.—Two theories have been advanced respecting the arrangement of the elements in fulminating gold. In the one,

put forth for the first time by Proust and Berthollet, this compound is considered as a pure and simple combination of oxide of gold and of ammonia; in the other, proposed in 1830 by M. Dumas, fulminating gold is considered as a combination of nitruret of gold and of ammonia, the nitruret of gold acting the part of an acid. It appears to me that the opinion of Proust and Berthollet harmonizes better with the facts. The circumstances which induce me to think so are the following:—1st. As many kinds of fulminating gold may be obtained as there are known oxides of gold. In M. Dumas's opinion therefore we must admit as many corresponding nitrurets of gold. Now up to this time it has not been possible to prepare any combination of gold with nitrogen. 2nd. The different kinds of fulminating gold present the same colour as the oxide of gold from which they are formed; which leads to the supposition that the oxides of gold enter into these combinations, without undergoing any alteration in their nature. 3rd. The analyses made by M. Dumas entirely agree with this view of the question. Thus M. Dumas represents the constitution of fulminating gold obtained with tritoxide of gold by the formula $(Au^2 N) + (NH^3) + H^3 O^3$.

It is evident that this formula may be reduced to this:—$Au^2 O^3 + 2(NH^3)$, that is to say, a subaurate of ammonia.

Fulminating gold obtained from chloride of gold furnished M. Dumas with numbers corresponding exactly to the formula $Au^2 O^3 + 2(NH^3) + HO$, that is to say, to the preceding hydrated compound.—*Comptes Rendus*, April 29, 1844.

On the Constituents of the Smoke of Tobacco. By M. Melsens.

In our notice of M. Zeise's researches on this subject (p. 10 of the present volume), it will be observed that he does not mention the occurrence of *nicotine* among the products resulting from the dry distillation of tobacco; from the experiments of M. Melsens, however, it appears that this principle is present in considerable quantity. He used in his experiments strong Virginian tobacco, filled the bowl of a porcelain pipe with the cut leaves, and then connected it with several Woulf's flasks, the first of which was empty, the second contained some water, the third and fourth dilute sulphuric acid; the smoke was drawn through these flasks by means of an aspirator.

A brown, alkaline, aqueous liquid, possessing a most disagreeable smell, effervescing with acids, and disengaging ammonia when treated with caustic potash, condenses in the first two flasks along with a quantity of a semifluid, tarry product, which dissolves in alcohol. The sulphuric acid in the last flask is coloured almost black, the odour is not so intense, and the tarry constituents are more solid and resinous. Some tar also collects in the tube leading to the aspirator.

The aqueous liquid in the first flasks is extremely poisonous according to some experiments made on dogs. If it be saturated with an acid, the tarry substances separated by filtration, lime-milk added

to the filtered solution, then submitted to distillation, the alkaline distillate saturated with an acid and evaporated, a brown liquid is obtained after removing some tarry flakes, from which caustic potash disengages a considerable quantity of ammonia, and separates a light oily liquid, which is dissolved in æther, and rectified after removal of the latter by distillation over burnt lime in a current of hydrogen. This liquid is nicotine. The first analysis afforded somewhat less carbon and hydrogen than M. Barral obtained; it was therefore treated with potassium until this retained its metallic lustre, and rectified over caustic barytes in a current of hydrogen, setting aside the first and last portions. It now afforded—

Carbon	74·3	10 =	750·0	74·1
Hydrogen	8·8	7 =	87·5	8·6
Nitrogen		1 =	175·0	17·3
			1012·5	100·0

This formula contains 1 equiv. less hydrogen than the formula of Barral and Ortigosa, and differs only by 1 equiv. of carbon from the formula for aniline or crystalline. When aniline is submitted to oxidation, its peculiar odour disappears, and on treating the residue with caustic potash a distinct odour of nicotine is disengaged. It would be interesting to ascertain more positively whether nicotine is formed by the oxidation of aniline.

The author obtained 30 grs. of nicotine from 9 lbs. of tobacco, which proves that the nicotine must have partially originated at the decomposition of the tobacco, since M. Barral procured only 16 grms. of pure nicotine from 40 lbs. of tobacco.

The tarry products afforded on distillation with much water a light, brown, sharp empyreumatic oil, and a black, pitchy residue, soluble in alcohol. The oil, when dehydrated over chloride of calcium and rectified, boils at 284° Fahr., but its boiling-point rises gradually to 572°, in which operation the oil gradually becomes yellow, green, and at last again brown, and loses its original odour. —*Ann. de Chim. et de Phys.*, t. ix. p. 465.

On the Essential Oil of Sassafras. By M. Saint-Evre.

The commercial oil extracted from the wood of *Laurus Sassafras* is a slightly yellow-coloured liquid, of an acrid taste, and a smell which resembles fennel oil. Its density is 1·09 at a temperature of 50°; submitted to distillation, it begins to disengage vapours at about 233° Fahr. The point of ebullition then rises rapidly to 442°, where it remains stationary until the greater part of the liquid has passed over.

This oil, thus prepared, submitted to elementary analysis, gave the following results:—

Carbon	72·0
Hydrogen	6·6
Oxygen	21·4

On causing bromine to act on the essence, a crystallized product is obtained; but since the analysis of this product, prepared with the same oil, presented considerable differences, it became probable that a mixture of two oils had been operated on, and it was consequently necessary to separate them; moreover, by passing a current of pure and dry ammoniacal gas through the distilled essence, a liquid free from nitrogen is obtained, which crystallizes on cooling and on spontaneous evaporation in large prisms. The analysis of these last crystals gave the following results:—

Carbon	73·03	73·30
Hydrogen	6·15	6·22
Oxygen	20·82	20·48

From the increase in carbon and absence of nitrogen, I was induced to submit the oil to a more intense cold by placing it in a mixture formed of 12 parts of ice, 5 of salt and 5 of nitrate of ammonia. At first it became opake, and on leaving it to itself in the refrigerating mixture for five or six hours, the vessel which contained it was found lined with large crystals of a perfect white colour; they were immediately pressed between double pieces of blotting-paper, melted and crystallized a second time by the same means, and the product was then ready for analysis.

These crystals, analysed with the greatest care, gave the following results:—

		Equiv.
Carbon	74·07	20
Hydrogen	6·17	5
Oxygen	19·76	2
	100·00	

Action of the Bromine.—On pouring a suitable quantity of bromine over the essence of sassafras, a somewhat violent reaction takes place; abundant vapours of hydrobromic acid are disengaged, and when they cease the oil suddenly solidifies to a crystalline mass.

These crystals correspond to the formula $C^{20}\,\frac{H}{Br^4}\,O^2$, which gives—

		Equiv.
Carbon	15·42	20
Hydrogen	0·25	1
Bromine	80·20	4
Oxygen	4·13	2
	100·00	

Comptes Rendus, April 15, 1844.

On the Hydruret of Copper. By Ad. Wurz.

In examining the action of hypophosphorous acid on salts of copper, I noticed under certain circumstances the formation of a hydruret of copper, which possesses all the characters of a definite compound. It may be prepared as follows;—

10 parts of hypophosphite of barytes is dissolved in water, and the barytes entirely precipitated by sulphuric acid; to the filtered liquid eight parts of sulphate of copper, dissolved in as little water as possible, is added. The mixture is heated gently at a temperature which should not exceed 158°. The liquid acquires a green colour, and then a precipitate forms, which at first is yellow, but gradually becomes darker until it presents the colour of mineral kermes. At this point of the operation there is frequently observed a disengagement of small bubbles of hydrogen; it is then requisite to cool the vessel immediately. The cold liquid is filtered, and the deposit washed in an atmosphere of carbonic acid with water deprived of air, and then dried by pressing it between sheets of blotting-paper.

The dry hydruret of copper inflames in chlorine, with production of dense vapours, which condense into flakes of perchloride of copper. This incandescence is equally perceptible on projecting it into bromine.

Hydrochloric acid has a very remarkable action on the hydruret of copper; when concentrated a lively effervescence takes place even in the cold, with formation of protochloride of copper. If too great an excess of acid has not been employed, this salt crystallizes partly in small laminæ, which are readily distinguished in the midst of a small residue of copper. On the addition of a little water the liquid becomes milky; otherwise it presents all the characters of protosalts of copper. From this it is evident that both the hydruret of copper and the hydrochloric acid are decomposed. I have verified this fact by direct experiments, decomposing the hydruret of copper by heat only, and then by hydrochloric acid. In the second case, I have always obtained from the same quantity of substance a double volume of hydrogen gas. Now it is known that hydrochloric acid acts with great difficulty on copper, and the presence of hydrogen, far from facilitating this action, should, according to the laws of affinity, add a new obstacle. The decomposition of the hydruret of copper by hydrochloric acid appears therefore to be effected by contact.

Two analyses, made with different samples, gave the following numbers:—

			Calculated according to the formula	
			Cu^2H*	Cu^8H^3
Copper	98·78	98·771	98·446	98·830
Hydrogen	1·22	1·229	1·554	1·170

Taking for basis the preceding analyses, the copper in the hydruret of copper is combined with about twelve hundred times its volume of hydrogen.—*Comptes Rendus*, April 15, 1844.

Green Urine.

Dr. Wenzel observed in a female patient, aged 25, suffering from obstruction of the gall-ducts with black bile, and chronic spasms resulting from it, that the urine during forty-eight hours was of a

* H = 12·5.

dark green colour, and contained more fatty matter, and was thicker than ordinary. It contained no sediment, but numerous dense clouds were suspended in it, resembling water filled with confervæ. No other peculiar symptoms were observed during the period.—*Med. Zeit.*, 1843, No. 12.

Researches on Narcotine and the Products of its Decomposition. *By* Prof. Wöhler.

[Continued from p. 252.]

7. *Hemipinic Acid* is formed by the higher oxidation of opianic acid. Its composition is represented by the formula $C^{10} H^4 O^5 + HO$. 1 atom of opianic acid gives rise therefore, by the assimilation of 1 atom of oxygen, to 2 atoms of hemipinic acid. This oxidation is effected by heating opianic acid, or narcotine itself, with hyperoxide of lead and dilute sulphuric acid; it is, however, difficult to arrange the proportions so that the hemipinic acid is not itself decomposed. It was also obtained by the action of manganese on a solution of narcotine, in an excess of hydrochloric acid.

Hemipinic acid crystallizes in colourless quadrilateral prisms, with rhombic base and oblique terminal surface. The crystals contain 2 atoms of water, which are expelled below 212°. It has only a faint taste, and is far more soluble in water than opianic acid; it melts at 356°, and sublimes like benzoic acid in shining laminæ. It forms an easily-soluble crystalline salt with ammonia; its silver salt is insoluble, and is obtained as a white pulverulent precipitate, the composition of which is represented by the formula $AgO + C^{10} H^4 O^5$.

8. *Cotarnine*, a new organic base, which is formed at the same time as opianic acid from narcotine. It contains the nitrogen of the narcotine. The reddish-yellow liquid, from which the opianic acid has subsided, is treated with chloride of platinum or chloride of mercury; the precipitated double salt decomposed by sulphuretted hydrogen, and the muriate of cotarnine thus obtained by hydrate of barytes.

Cotarnine is obtained as a radiately-crystalline dark yellow mass; it dissolves readily in alcohol and in water with a deep yellow colour; it has a very bitter taste, and reacts faintly alkaline. On exposure to heat, it melts, and is carbonified with evolution of a very disagreeable odour; its combination with muriatic acid is amorphous. It is precipitated from the muriatic solution both by tannic acid as well as by chloride of platinum and chloride of mercury. The double salt with platinum is reddish-yellow and crystalline, the double salt with mercury is of a pale yellow colour and very crystalline; both dissolve in hot water, but appear to undergo some change by its long-continued action. From the analysis of these salts it appears probable that cotarnine is $C^{26} H^{13} NO^5$. However, its composition still requires more accurate determination.

If Regnault's formula for the composition of narcotine, $C^{48} H^{24} N O^{15}$, be adopted, this, on its decomposition by the hyperoxide of manganese, would assimilate 6 atoms of oxygen, and form—

1 atom of cotarnine.....	=	$C^{26} H^{13} N O^{5}$
1 atom hydrated opianic acid....	=	$C^{20} H^{9} O^{10}$
2 atoms carbonic acid.....	=	$C^{2} O^{4}$
2 atoms water.....	=	$H^{2} O^{2}$

1 atom narcotine	$= C^{48} H^{24} N O^{15}$	$= C^{48} H^{24} N O^{21}$
+ 6 atoms oxygen	$= O^{6}$	

9. ***Humopinic Acid*** is a product of the decomposition by heat of narcotine, which, on being melted and exposed to a temperature of 428°, is suddenly decomposed, with considerable tumescence, into ammoniacal gas and a brown vesicular substance, which consists principally of humopinic acid. It was purified by digestion in boiling dilute muriatic acid, solution in caustic potash, and precipitation by muriatic acid.

Humopinic acid is a dark brown amorphous substance, which melts on exposure to heat, and burns with a luminous flame, diffusing an odour resembling narcotine. It is perfectly insoluble both in dilute acids and in water, but is dissolved by alcohol with a deep yellow-red colour. It forms with the alkalies saffron-yellow solutions, which give dark brown gelatinous precipitates with salts of barytes and lead. When humopinic acid is boiled for some length of time with water, it is rendered insoluble in ammonia; and on its solution in potash or in alcohol, it leaves behind a blackish-brown body, which is probably humine. The analyses have left it doubtful whether the humopinic acid is $C^{48} H^{23} O^{17}$ or $C^{40} H^{20} O^{14}$. The first is based upon Regnault's formula for narcotine, the latter upon Liebig's, on the supposition that 1 equiv. ammonia separates from the narcotine at its formation, and that it has assimilated 2 atoms of water on its treatment with alkali.

There moreover constantly occurs in the crude humopinic acid, another base, probably a secondary product, which is decidedly distinct from narcotine and cotarnine, but has not yet been more closely examined. It affords crystalline double salts with chloride of platinum and chloride of mercury.

10. *Apophyllenic Acid*, a nitrogenous acid. It was obtained only once, and is probably a product of decomposition of the cotarnine. It forms with water of crystallization colourless, well-defined rhombic octahedrons, which split readily parallel with the base, and with mother-of-pearl lustre; they part with their water below 212°, and become milk-white; they dissolve very slowly and with difficulty in water. This acid crystallizes in a different form, without water of crystallization, from a boiling-hot saturated solution. It has a faintly acid, somewhat astringent taste, melts on exposure to heat, and is carbonified with evolution of an alkaline oily body, which, judging from its odour, is nothing further than chinoline. Its ammonia salt crystallizes. It is not precipitated by salts of barytes or salts of lead, but its silver salt separates after a few minutes in delicate white acicular crystals, aggregated in spherical groups: on exposure to heat it deflagrates with as much liveliness as oxalate of silver.

11. *Action of Hydrate of Potash on Narcotine.*—Narcotine undergoes a remarkable change when heated with a very concentrated solution of caustic potash, without, as it appears, parting in any manner with carbon or nitrogen; it is evidently converted into an electro-negative body capable of combining with bases, but which so readily passes back into narcotine, that hitherto all attempts to isolate it have failed. This change most probably depends on the separation of the elements of water, by the reassimilation of which narcotine is again formed. The name of narcotic acid may be applied to this substance.

The potash salt is formed when narcotine is boiled for some time with a very concentrated solution of caustic potash, with frequent shaking. The narcotine melts to a yellowish oily body, which subsides, and which retains this form on cooling, and after pouring off the caustic ley. It is now very readily soluble in water; the solution has a very bitter taste; when warmed it becomes turbid, and on boiling deposits a voluminous precipitate of minute acicular crystals, which are unaltered narcotine. It requires, however, long-continued boiling and considerable dilution before the whole of the narcotine is restored in this manner. The liquid then contains free potash and a small quantity of a yellow colouring substance, which without doubt is a secondary product which has originated through the influence of the atmosphere. Narcotate of potash is likewise very readily soluble in alcohol, and remains unaltered in this solution; on evaporation it is left as an amorphous mass. When water is added to this solution, it deposits after a time crystallized narcotine. If the aqueous solution be mixed with an acid, a salt of narcotine is immediately formed. Salts of barytes and lime are not thrown down by it; but it forms with acetate of lead a very voluminous pale yellowish precipitate, which is soluble in alcohol. Two crystalline bodies were obtained on decomposing this solution by sulphuretted hydrogen; the one was narcotine, the other was converted into narcotine in all the experiments which were made to isolate it. This lead compound contained nearly 38 per cent. oxide of lead, from which the number 2284 results as the atomic weight for narcotic acid, being about half that of narcotine = 4673. It is possible therefore that the atom of narcotine may have been separated by the action of the base into 2 atoms of narcotic acid. If we assume that the elements of 2 atoms of water are set free at the same time, the atomic weight of the narcotic acid would be 2224, which approximates closely to the number found.—*Götting. gelehrt. Anzeigen*, March 28, 1844.

ANALYTICAL CHEMISTRY.

On the Detection of Lithia by the Blowpipe when Soda is present. By W. Stein.

The reaction of soda before the blowpipe conceals, as is well known, that of lithia, but it has not been ascertained to what extent.

The author mixed various quantities of chloride of sodium and chloride of lithium, and found that the soda-flame became darker as the amount of chloride of lithium increased; so that when the proportion was 1000 chloride of lithium to 1 chloride of sodium, it was sufficiently orange to prevent its being considered as pure soda, and that with 2000 chloride of lithium to 1 chloride of sodium it was distinctly red. With this proportion every one, with a little practice, will readily recognise the presence of lithia. This however holds good only when, as usually happens, the sample is held at the point of a luminous flame of a tallow-candle. Experience has shown that the result differs when the process is varied, and that with some little practice the presence of lithia may be distinctly detected in a mixture consisting of equal parts of chloride of sodium and chloride of lithium, in the following manner:—The point of the blowpipe is held above the centre of the flame of a tallow-candle, the wick of which is cut short; in this manner a very small flame is produced, the inner portion of which is almost of a pure blue. After having heated the sample in the outer flame, it is immediately conveyed into the middle of the blue flame, when there is instantly observed either a red colouring of the margins of the flame, or a small conical red-coloured flame at the extremity of the blue flame. This reaction does however not last more than an instant, when the soda colour again makes its appearance.

This is apparently owing to the chloride of lithium alone being volatilized at first by the lower temperature of the blue flame, while the chloride of sodium requires a longer-continued heating. This induced the author to operate altogether at a lower temperature. The sample was therefore held in the flame of the candle without blowing on it, which however did not suffice; but a very satisfactory result was obtained on immersing the sample melted on the wire, while still warm, into the tallow, then holding it in the middle of the flame to set light to it, and carefully observing the flame. While burning brightly, it was surrounded by a very distinct red margin, when the proportion did not exceed 100 chloride of lithium to 1 of chloride of sodium, and on the slow extinction of the flame it became broader and very evident. The red margin, on the extinction of the flame, was, although faint, still perceptible with a mixture consisting of 1000 chloride of sodium and 1 of chloride of lithium, which therefore contained only 1 lithium to 2580 sodium. With a still greater proportion of sodium and lithium, it appears no longer possible to detect the latter by the above method. For the success of the result, it should be observed that the sample should not, if possible, be perfectly fused, but still slightly porous, so as to absorb some of the melted tallow, and that it should be held in the middle of the flame and set light to as quickly as possible. The sulphate behaves precisely similar to the chloride of lithium. No other combinations were examined.

This method may perhaps be employed with advantage for detecting lithia in the analysis of mineral waters, after the greater portion of the salts of soda have been removed either by crystal-

lization or treatment with weak alcohol.—*Journ. für Prakt. Chem.*, xxxi. pp. 361–364.

Aqueous Infusion of Galls as a Test.

This is best prepared, according to M. Pettenkofer, by infusing 1 part of pounded galls in 3 to 4 parts of water, allowing it to stand for several hours, straining, submitting the residue to pressure, adding to the turbid liquid 2 parts common salt, and separating by filtration the glutinous precipitate which is produced. This liquid retains its transparency and power of precipitating gelatine for years.—Buchn. *Repert.*, xxxiii. p. 88.

Test for Strychnine.

In a former Number (vol. i. p. 629) we noticed the new test proposed by E. Marchand for the detection of minute quantities of strychnine. The importance of this subject in medico-legal inquiries induces us to give the following satisfactory confirmation accorded to it by Drs. Erdmann and Marchand. They state that they found the reaction very beautiful and distinct on employing pure strychnine, even when the quantity of the alkaloid was extremely minute. With a mixture of 12 grms. of milk and ½ milligramme of strychnine, peroxide of lead produced, in the liquid filtered from the coagulated caseine, a distinctly red colour, which at first possessed a slight violet tint. They moreover observe that it is not advantageous to employ the sulphuric acid in a concentrated state, but diluted with about one-fourth water.—*Journ. für Prakt. Chem.*, April 1844.

CHEMICAL PREPARATIONS.

Observations on Tooth Powders. By Dr. Heider.

The author, who is a practical dentist of great celebrity in Vienna, has published the following observations respecting the preparation of tooth powders, which may not be uninteresting to some of our pharmaceutical readers:—

Among the constituents of a good tooth powder the first in importance is charcoal, and especially *lime-tree charcoal*. It forms a very soft and cheap powder, and moreover possesses the valuable property of absorbing colouring substances and destroying the disagreeable odour produced by carious teeth. Small quantities, left in the spaces between the teeth, have a disinfecting action on the particles of food which collect there. It does not, it is true, possess a pleasing colour, and is on that account rejected by many; moreover, particles sometimes accidentally get in between the teeth and gums, and shine through with a bluish colour.

Next to it in importance is carbonate of magnesia, both on account of its absorbent power and its extreme softness. Its property of neutralizing acids deserves particular attention, and from its white colour any pleasing tint may be readily imparted to it by some harmless colouring substance.

The *lapides cancrorum* and *creta alba præparata* resemble the carbonate of magnesia in their chemical behaviour and in their action. *Ossa sepiæ, conchæ præparatæ, corallia alba et rubra* are, as carbonate of lime, insoluble, like the two preceding, in the secretions of the mouth; but they are less soft, and should therefore only be employed by grown-up persons, and even then should be mixed with other powders.

Ashes are less to be recommended; they are sometimes even injurious, for in them the alkali is not neutralized by carbonic acid. Soap in which the alkali is combined with fatty acids deserves the preference, and were it not for its disagreeable taste, it would form an excellent ingredient for tooth powders.

Orris-root is a harmless substance, and is generally added to most tooth powders on account of its agreeable odour. Many of the ingredients most frequently mixed with tooth powders, such as alum, cream of tartar, tartaric and citric acids, borax, chloride of lime, &c., are absolutely injurious, and should always be rejected.

The most usual colouring substances employed are carmine, florentine lac, *sanguis draconis, bolus armeniaca, corallia rubra, coccinella, lignum Santali rubrum*; but only the first two give a beautiful colour in small quantities.

To please the organs of smell and taste, a few grs. of vanilla, or a couple of drops of an essential oil, such as bergamot, neroli, rose oil, oil of cloves, oil of peppermint, may be added.

With respect to the mode of application, it is recommended to clean the teeth in the evening, before going to rest, with a *soft* brush and some powder; otherwise the particles of food have time during the night to undergo putrefaction, and when removed in the morning may have already produced considerable injury.

Prof. Carabelli used to prescribe a gray tooth powder in the following form:—

℞ Pulv. oss. Sepiæ,
Lapid. Cancrorum ana unc. unam et semis;
Corticis Cinnamomi,
Iridis florentinæ,
Carb. Lign. Tiliæ ana drachm. tres;
Vanillæ grana decem.—Misce.

For a less expensive powder, calcined oyster-shells might be employed instead of *os sepiæ*, and a few drops of bergamot oil instead of vanilla. He objected to red tooth powders, from its being impossible to observe when the gums bleed.

For children and young people, carbonate of magnesia, without any other addition, is most to be recommended, because, on account of its softness, it is not liable to injure the still weak enamel, and at

the same time it neutralizes the acid which frequently occurs in the secretions of the mouth in children.—*Oestr. Medicin. Wochenschrift.*

Preparation of Mercurial Ointment.

M. Heusler recommends the following method:—6 oz. of mercury, 2 oz. of suet and 6 oz. of lard are rubbed together in a shallow iron mortar, with the addition of about a drachm of sulphuric æther at intervals, until all globules have disappeared.

The process occupies about three-quarters of an hour, and the quantity of æther required is about 7 drachms.—*Jahrb. für Prakt. Pharm.*, vii. p. 370.

Aqua Sinapis.

According to M. Heusler, by the distillation of 18 oz. of coarsely-powdered black mustard, with 8 oz. of alcohol, and sufficient water until 36 oz. have passed over, a liquid is obtained, which, when applied to the skin on linen moistened with it, acts more quickly and powerfully than an ordinary mustard-poultice.—*Jahrb. für Prakt. Chem.*, vii. p. 368.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Energiatype, a new Photographic Process. *By* Robert Hunt.

While pursuing some investigations, with a view to determine the influence of the solar rays upon precipitation, I have been led to the discovery of a new photographic agent, which can be employed in the preparation of paper with a facility which no other sensitive process possesses. Being desirous of affording all the information I possibly can to those who are anxious to avail themselves of the advantages offered by photography, I solicit a little space in your columns for the purpose of publishing the particulars of this new process. All the photographic processes with which we are at present acquainted, sufficiently sensitive for the fixation of the images of the camera obscura, require the most careful and precise manipulation; consequently, those who are not accustomed to the niceties of experimental pursuits are frequently annoyed by failures. The following statement will at once show the exceeding simplicity of the new discovery.

Good letter-paper is first washed over with the following solution:—

A saturated solution of succinic acid....	2 drachms.
Mucilage of gum-arabic.....	½ ...
Water.....	1½ ...

When the paper is dry, it is washed over once with an argentine solution, consisting of 1 drachm of nitrate of silver to 1 oz. of distilled water. The paper is allowed to dry in the dark, and it is

fit for use. It can be preserved in a portfolio, and at any time employed in the camera. This paper is a pure white, and it retains its colour, which is a great advantage. At present I find it necessary to expose this prepared paper in the camera obscura for periods, varying with the quantity of sunshine, from two to eight minutes, although, from some results which I have obtained, I am satisfied that, by a nice adjustment of the proportions of the materials, a much shorter exposure will suffice. When the paper is removed from the camera, no trace of a picture is visible. We have then to mix together 1 drachm of a saturated solution of *sulphate of iron* and 2 or 3 drachms of the *mucilage of gum-arabic*. A wide flat brush, saturated with this solution, is now swept over the face of the paper rapidly and evenly. In a few seconds the dormant images are seen to develope themselves, and with great rapidity a pleasing *negative* photographic picture is produced. The iron solution is to be washed off as soon as the best effect appears, this being done with a soft sponge and clean water. The drawing is then soaked for a short time in water, and may be permanently fixed by being washed over with ammonia, or perhaps better with a solution of the hyposulphite of soda, care being taken that the salt is afterwards well washed out of the paper. From the pictures thus produced, any number of others, correct in position and in light and shadow, may be produced, by using the same succinated papers in the ordinary way, from five to ten minutes in sunshine producing the desired effect.

The advantages which this process possesses over every other must be, I think, apparent. The papers are prepared in the most simple manner, and may be kept ready by the tourist until required for use. They require no preparation previously to their being placed in the camera, and they can be preserved until a convenient opportunity offers for bringing out the picture, which is done in the most simple manner, with a material which can be anywhere procured.

Anxious to give the public the advantage of this process during the beautiful weather of the present season, I have not waited to perfect the manipulatory details which are necessary for the production of portraits. It is sufficient, however, to say, that experiment has satisfied me of its applicability for this purpose.

Prismatic examination has proved that the rays effecting this chemical change are those which I have elsewhere shown to be perfectly independent of solar light or heat. I therefore propose to distinguish this process by a name which has a general rather than a particular application. Regarding all photographic phænomena as due to the principle *Energia*, I would nevertheless wish to distinguish this very interesting process as the *Energiatype*.

I inclose you a few specimens of the results already obtained. The exceeding sensibility of the Energiatype is best shown by an attempt to copy engravings or leaves by it. The three specimens I inclose were produced by an exposure of considerably less than one second.—*Athenæum*.

Cement for Iron Steam Pipes.

Good linseed-oil varnish is triturated with a mixture of equal parts of white lead, manganese and white pipe clay until it has acquired the desired consistence. This cement becomes as hard as stone.—*Journ. für Prakt. Chem.*, xxx. 5.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

April 1, 1843. (The President in the Chair.) The following communications were read:—

"On some Salts of Meconic Acid," by John Stenhouse, Ph.D.

Dr. Stenhouse in this paper states that the meconic acid employed in these experiments was prepared by Robiquet's process as modified by Gregory. Its composition was—

Carbon	42·45
Hydrogen	2·07
Oxygen	55·48

Meconate of Lead was formed from the neutral acetate of lead. Its analysis gave—

	Atoms.	
Carbon	14	16·23
Hydrogen	3	0·57
Oxygen	13	19·72
Oxide of lead	3	63·48

This salt is tribasic, with 2 atoms of water, and its formula $\overline{Me} + 3PbO + 2aq$.

Meconic Acid and the Persalts of Iron.—When meconic acid is added to a solution of any of the persalts of iron, it immediately assumes a blood-red colour. Even when concentrated, it may be kept any length of time without its giving any precipitate. When a solution of meconic acid is first neutralized with ammonia, and then treated with a slight excess of neutral persulphate of iron, a fine bright crimson precipitate appears after standing for a few hours. When dried at 212° and analysed, it gave, according to the fifth experiment—

Carbon	31·44
Hydrogen	2·30
Oxygen	39·72
Nitrogen	3·49
Fe^2O^3	23·05

The compound is evidently a double salt, consisting of meconate of iron and meconate of ammonia.

Iron Salt from Æthereal Solution of Meconic Acid.—Upon

adding a saturated solution of meconic acid in anhydrous æther to a solution of perchloride of iron in anhydrous æther, the solution is of a deep red colour, and in a few minutes a quantity of reddish-brown flocks precipitate. When dried, they formed a reddish-brown powder. Dried at 212° its analysis gave—

Carbon	26·03
Hydrogen	1·74
Oxygen	41·41
Fe^2O^3	30·82

Komenic Acid.—This acid was prepared by boiling meconate of lime in a great excess of strong muriatic acid. This removes almost the whole of the base, and converts the meconic into komenic acid. Dr. Stenhouse then states the mode of purifying this acid.

Komenate of Ammonia.—This salt was formed by adding a slight excess of ammonia to a hot solution of komenic acid. It crystallized, and was of a slight shade of yellow. When dried at 212°, it gave, according to Dr. Stenhouse's analysis—

	Atoms.	
Carbon	12	41·86
Hydrogen	7	4·25
Oxygen	10	45·85
Nitrogen	1	8·04

The salt is therefore the acid komenate of ammonia, with 1 atom water of crystallization. Its formula $\bar{K}o + NH^3 + HO + 1$ atom aq.

Komenate of Lead.—This salt was prepared by adding excess of neutral acetate of lead to komenic acid. A whitish granular precipitate fell, which, when collected and dried at 212°, gave upon examination—

	Atoms.	
Carbon	12	19·14
Hydrogen	4	1·16
Oxygen	10	21·20
PbO	2	58·50

This salt is therefore bibasic, with 2 atoms water, and its formula is $C^{12}H^2O^8 + 2PbO + 2\,aq = \bar{K}o + 2PbO + 2\,aq$.

The salt made from acetate of lead and komenate of ammonia was also analysed, and gave 58·61 oxide of lead.

Komenate of Copper.—This salt was formed by adding sulphate of copper to a hot solution of komenic acid. A crystalline precipitate fell after some time of the colour of Schweinfurth green. When dried at 212°, its analysis gave—

	Atoms.	
Carbon	12	31·22
Hydrogen	8	1·85
Oxygen	10	33·56
CuO	2	33·37

This is a bibasic salt, with 2 atoms water. Its formula is $\bar{K}o + 2CuO + 2\,aq$.

Komenate of Silver.—Komenic acid forms two silver salts, both of which have been examined by Prof. Liebig. The monobasic is made by adding komenic acid to a solution of nitrate of silver. It forms a white powder. Its analysis gave 43·98 per cent. silver. Its formula is $\bar{K}oAgO + aq$. The yellow salt is formed by adding komenate of ammonia to nitrate of silver. It contains 62·46 silver.

"On the Hydrate of Laurel Turpentine," by Dr. Stenhouse.

Dr. Stenhouse, in continuation of a former paper on this substance, states that he obtained it in fine large rhombic prisms, which were perfectly white, and had neither taste nor smell. When dried at 212°, and subjected to analysis, it gave—

	Atoms.	
Carbon	5	70·30
Hydrogen	3	11·62
Oxygen	1	18·08

From which it is evident that the crystals are isomeric and isomorphous with those of the hydrates of the oils of turpentine and cedar. The most probable formula is $C^5H^4 + HO$, or 1 atom oil and 1 atom water.

When a portion of these crystals were distilled with anhydrous phosphoric acid, they yielded a colourless oil lighter than water, which had the same taste and smell as laurel oil, and appeared to be that oil regenerated.

"On East Indian Grass Oil," by Dr. J. Stenhouse.

Dr. Stenhouse states that this oil is said to be the produce of the *Andropogon Ivaracusa*, commonly called the oil of Namur. It has a very fragrant aromatic odour, resembling that of otto of roses. Its boiling temperature was 297° Fahr., but gradually rose to 320°, then remained stationary for some time, and then continued rising. Its analysis gave—

Carbon	87·76
Hydrogen	11·46
Oxygen	4·78

And evidently consisted of a carburetted hydrogen.

A quantity of the rectified oil was treated with small pieces of sodium. An evolution of hydrogen was caused thereby, which ceased in a short time, and the sodium which had not dissolved remained quite bright. This oil was rectified, and when subjected to analysis gave—

	Atoms.		Calculated.
Carbon	5	88·37	88·46
Hydrogen	4	11·50	11·54
		99·87	100·00

The affinity of this oil for oxygen appears to be very considerable as part of the oil cannot be distilled without some of it being converted into resin.

"On the Reduction of the Salts of Peroxide of Iron by Means of Vegetable Substances," by Dr. J. Stenhouse.

Dr. Stenhouse states that, in the course of some experiments, he had observed that some of the most common vegetable substances reduced the persalts of iron with great facility. Meadow-grass, twigs of trees and shrubs, hay, chips of wood and sawdust, peat and wood-charcoal, and all substances which he tried, had this effect. The persulphate of iron was reduced to the state of protoxide by some of the substances in less than twenty-four hours in the cold, but when heated, in the course of an hour or two. Sugar, starch, gum, spirits of wine and oil of turpentine, and pieces of paper, though they produce no effect in the cold, at a boiling temperature also caused the partial reduction of the salt.

"Observations on the Chemical and Pharmaceutical Characters of the Peruvian *Matico*," by John F. Hodges, M.D.

The author, after briefly observing on the employment of the leaves of the Matico as a medicine in Peru, and the observations already published on this subject, as also its botanical and physical characters, proceeds to detail the experiments which he has made with the view of determining its proximate constituents, and the preparations of it which will best exhibit its medical properties. The infusion, decoction, extract, tincture and volatile oil are individually treated on, and the action of various reagents on each of these preparations detailed. The latter is described as a heavy oil, of a light green colour, of the consistence of castor oil, becoming crystalline by keeping, its smell powerful, aromatic and permanent, having a strong camphoric taste, like a mixture of the oils of rosemary and cubebs. Dr. Hodges concludes from his experiments that the leaves of the Matico contain,—1st, chlorophylle; 2nd, a soft dark gum-resin; 3rd, a brown colouring matter; 4th, a yellow colouring matter; 5th, gum and nitrate of potash; 6th, a bitter principle, maticine; 7th, an aromatic volatile oil; 8th, salts; 9th, lignine. The cold infusion, from its containing all the active principles existent in the plant, Dr. Hodges considers as the best form for its medicinal employment.

PATENT.

Patent granted to Edmund Snell, *for Improvements in the Manufacture of Soap.*

This invention consists in mixing with the saponified fats or oils certain materials prepared from potatoes and other vegetable matters containing farinaceous substances.

The method of preparing these materials from potatoes is as follows:—The potatoes, after being washed, are reduced to a pulp in any suitable apparatus, from which the pulp is allowed to fall upon two inclined sieves or screens having a slight horizontal motion. At the top, and midway down the upper sieve (which is covered with wire-cloth of thirty meshes to the inch), are pipes, extending across

the sieve, and perforated with numerous holes, from which water issues; the coarse parts of the potatoes are, by this means, separated from the finer parts, and discharged into a vat; while the finer parts pass through the upper sieve on to the lower one (which has sixty meshes to the inch), where a further separation takes place, the coarse parts descending into the vat, and the finer parts, which the patentee calls *dextrine*, falling on to an inclined plane of wood placed beneath the lower sieve, but inclined in the opposite direction. The dextrine is conducted by the inclined plane into a vat, where it is repeatedly washed in sieves of finer wire-cloth until deprived of all its impurities; it then sinks to the bottom of the vat, and may be taken up in pails ready for use. The coarse part of the potatoes, termed *fibrine*, is washed in coarse sieves, and remains in a vat, covered with water, until it is wanted. If preferred, the dextrine may be dried, and kept until it is required for use; in this case, to each ton of saponified fat or oil an addition is made of from 3 to $3\frac{1}{2}$ cwt. of dextrine, which is first mixed with from 1 to $1\frac{1}{2}$ cwt. of cold water, and, after standing for an hour, 6 cwt. of nearly boiling water are added; it is then mixed with the soap in the manner hereinafter mentioned.

White soap is made by the patentee from tallow or oil and alkali, in a boiler heated by a steam jacket, using as much alkali as the tallow or oil will take up; and when the soap is in a fit state "to cleanse into a frame," he takes, for each ton of saponified matter, from $4\frac{1}{2}$ to 5 cwt. of dextrine, in its wet state, and adds thereto about 6 cwt. of boiling water, so as to make it into a thin paste. This paste, as soon as all the spent lye is pumped out of the boiler, is added to the soap, and, when properly mixed and heated, the soap may be cleansed into frames in the usual way. Yellow soap is made in a common soap-pan, with tallow or oil and alkali, and either with or without resin; after the soap is "fitted," it is heated in the boiler before mentioned, and the above quantity of dextrine is added in the manner described. If no resin is put in the soap, a much larger quantity of dextrine may be used; and it may be added either with or without "fitting" the soap.

When fibrine is used in the manufacture of common soap, as much water is taken from it as will leave a thick body, which is then put into a boiler, heated by steam, together with an equal quantity of tallow or oil and resin, alkali is added in the usual way, and the whole is boiled until it is ready to be cleansed into frames.

Common soap, made in the ordinary manner, and containing a large quantity of alkali, may be re-melted, and dextrine added thereto, for the purpose of improving its colour, and preventing it from wasting so fast in hot water as it would otherwise do.—Sealed Nov. 21, 1843.

THE CHEMICAL GAZETTE.

No. XLI.—July 1, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Cholic Acid, Choloïdic Acid, and Product obtained from Ox-bile by means of Oxidizing Agents, with some Remarks on the Formula for Proteine. *By* Geo. Kemp, M.D., Cantab.

Next in importance to the determination of the chemical composition of a body by actual analysis, must be ranked those analogous bodies obtained by the operation of agents which effect changes easily observable and readily traced. Whilst the former, by comparison of the ratio of the elements respectively with the combining weight, also ascertained, furnishes us with an accurate expression or formula for the body as a whole, the latter, taken collectively, must as certainly represent the original mass, as the sum of the parts is equal to the whole.

Some of the most interesting of the changes alluded to, and invaluable as the means of solving various abstruse problems, particularly in animal chemistry, are effected by means of the action of caustic alkalies and acids containing a large relative proportion of oxygen; under both of which circumstances, however, we may, to a certain extent, consider a powerful oxidation as the cause of the results observed.

During the action of caustic potash, for instance, on a body containing the four organic elements, we obtain, on the one hand, carbonic acid, on the other, ammonia, as the result of the decomposition of the hydrate water of the alkali. A good illustration of this is afforded in the production of cholic acid by digesting ox-bile in a strong solution of caustic potash. This interesting body seems to have been first discovered by Gmelin, and subsequently prepared by Demarçay, in a manner described at length by Berzelius (ix. p. 279). Some discrepancy is observable in the description of the body as prepared by the two philosophers. Gmelin*, by destructive distillation, obtained an ammoniacal fluid, a certain indication of the presence of nitrogen. Dumas, on submitting Demarçay's preparation to ultimate analysis, found that element entirely wanting. Comparatively recent researches afford a clue to explain, in a very probable manner, the cause of this circumstance. In the examina-

* Berzelius, ix. p. 278–280.

tion* of the elementary composition of the mucus of the gall-bladder, that secretion was found to contain 15 per cent of nitrogen, and to be in fact a proteine-compound; now, by the action of caustic potash on proteine, it was found by Mulder to be resolved, besides other bodies, into leucine, protide and erythroprotide, each of which contains upwards of 10 per cent. of nitrogen. Provided therefore that the mucus is not carefully removed from the ox-bile previous to digestion in caustic potash, the presence of nitrogen in the new derivatives is inevitable.

In a former Number of this Journal a formula was proposed for the electro-negative body, which in combination with soda forms the principal portion of the ox-bile, as follows:—$C^{48}\,H^{42}\,N\,O^{13}$; and if this formula be correct, or even approximating to the truth, we must be able to establish a very evident relation between this formula and that expressive of cholic acid. Now the formula for this body has been differently stated; according to Dumas, $C^{42}H^{36}O^{10}$; according to Liebig†, $C^{74}\,H^{60}\,O^{18}$. We must however observe that both of these formulæ are merely empirical, and not founded on a combining weight decided by experiment; they must, therefore, to use the language of Berzelius, be "in a high degree unsafe." In order to remove any doubt on the subject, I prepared a portion of this acid with the greatest possible care, combined it with oxide of silver, and thus estimated its equivalent weight.

358 millegrammes of the silver salt, burnt in a porcelain crucible, gave metallic silver = 0·122.

And 122 : 358 :: 1350‡ : 3961.

Considering this body as containing 2 equivalents of base to 1 of acid, we obtain the combining weight = 5022; and if we subtract 1 equivalent of carbonate of ammonia from the proposed formula for the electro-negative body in the ox-bile, we have—

$$(C^{48}\,H^{42}\,N\,O^{13}) - (CO^2 + NH^3) = C^{47}\,H^{39}\,O^{11}$$
$$= 5111.$$

But the results of the analysis of the cholic acid by Dumas are in 100 parts—

		Calculated as $C^{47}\,H^{39}\,O^{11}$§.
Carbon	68·5	68·9
Hydrogen	9·7	9·5
Oxygen	21·8	21·5

a circumstance which strongly confirms the correctness of the formula I have proposed for the ox-bile. On no consideration however can Liebig's formula, $C^{74}\,H^{60}\,O^{18}$, be supported as a rational formula.

With reference to the choloïdic acid, the same sources of uncertainty and error exist as we have hitherto witnessed with reference to

* Kemp, "Ueber die Zusammensetzung des Schleims."—*Annalen der Chemie*, vol. xliii. p. 117.

† Animal Chemistry, p. 349.

‡ Marignac's equivalent number for silver.

§ Carbon = 75.

cholic acid; no equivalent number was, or could be determined by Demarçay on repeated trials. Now, on treating ox-bile with sulphuric acid, I have obtained, in addition to the choleic acid of Demarçay, a body resembling in its physical characters the choloïdic acid of Demarçay; and on deducting from my formula for ox-bile the formula for Demarçay's choleic acid, we obtain a formula accurately expressive of the results of his analysis of choloïdic acid; thus—

$$(C^{48}H^{42}NO^{13})^{*} - (C^{42}H^{37}NO^{12}) = C^{6}H^{5}O$$
$$= 612, \text{ giving—}$$

		Dumas found†
Carbon	73·5	73·3
Hydrogen	10·1	9·7
Oxygen	16·4	17·0

Although this circumstance is not by any means brought forward with the confidence of a fact proved by direct experiment, still, as a step in the chain of accumulative evidence, it cannot but be considered as admissible. The formula proposed by Liebig, $C^{36}H^{56}O^{12}$, will not bear examination, as it requires a whole per cent. more carbon than was obtained by analysis.

A few observations will suffice on the product of oxidation by means of nitric acid. When a solution of ox-bile, perfectly freed from mucus, is submitted to the action of this agent, copious red fumes are given off, and the ultimate result is an acid body free from nitrogen, of which I can at present furnish only the few following particulars; for although I made Professor Liebig acquainted with this body in 1842, I thought it more important to examine the bile of omnivorous and carnivorous animals before the respective products of decomposition; and the extent and difficulty of the research will, I am convinced, be an available apology with any person practically acquainted with the subject.

173 millegrammes gave CO^{2} = 0·410
HO = 0·132
or Carbon = 64·6 per cent.
Hydrogen = 8·4 ...

which, expressed by the formula $C^{48}H^{39}O^{15}$, gives—

Carbon	64·5
Hydrogen	8·7
Oxygen	26·8
	100·0

Now $C^{48}H^{39}O^{15} = [(C^{48}H^{42}NO^{13}) - (NH^{3})] + O^{2}$.

From this very cursory examination, therefore, it is apparent that the new body accurately expresses the electro-negative portion of

* Demarçay's formula is $C^{42}H^{36}NO^{12}$. I have taken the slight liberty with the hydrogen, in order to show the analogy, though $C^{42}H^{37}NO^{12}$ does in fact equally well express the results of the analysis.

† Berzelius, ix. p. 268.

the ox-bile deprived of its nitrogen in the form of ammonia, and oxidized by the agency of the nitric acid.

Having thus established the composition of the body by its ultimate analysis, by obtaining an equivalent number, by an examination of the products of decomposition, and by analogical reasoning in the case of choloïdic acid, it will, I am sure, be granted, by impartial, competent judges, that the course pursued has been a fairer and more philosophical one than suggesting theories first and bending facts to them afterwards.

Perhaps it might appear, to an ordinary reader of the researches which are now going on in animal chemistry, that the bile has been forced upon him *usque ad nauseam*; it must be remembered, however, that on its true composition depends the truth or falsehood of by far the greater number of the theories which Professor Liebig has advanced in his work on Physiology and Pathology. From an empirical formula of the bile, which has now been satisfactorily proved to have no foundation in truth, he has deduced a formula of proteine totally different from the facts of the case as elicited by Mulder; and, until the public mind is disabused on the subject, it will be a hopeless task to press upon its attention deductions which are calculated not only to solve some of the most intricate problems in physiology, but also to confer real benefit on mankind by an additional insight into the nature of morbid actions. The really well-informed and nature-seeking class of men, in all countries a small but chosen band, will attribute due importance to researches carried forward on right principles; and to such the honest labourer will never make a vain appeal for that consideration and forbearance which his imperfect labours may demand.

Douglas, Isle of Man, June 20, 1844.

On some new Salts formed by the Action of Sulphurous and Nitrous Acids on the Alkaline Bases. By M. E. Fremy.

When a current of sulphurous and of nitrous or hyponitrous acids is passed into a large excess of potash, the liquid immediately deposits long silky needles of a potash salt, which is almost insoluble in cold water. This salt contains a new acid, formed of oxygen, sulphur, and nitrogen; it undergoes a very characteristic decomposition by heat, being transformed into sulphate of potash, ammonia, and a volatile salt of ammonia.

The salts of soda and of ammonia can be prepared direct like the potash salt; they are soluble in cold water and crystallize easily. A solution made in the cold is neutral, and is not precipitated either by salts of barytes or of lead; when boiled it becomes strongly acid, and offers the reactions of sulphuric acid. The liquid contains an ammoniacal salt.

I believe that the preceding facts characterize sufficiently the new salts, which are formed in the reaction of sulphurous and nitrous acids on bases; these bodies will evidently have to be placed by the side of the nitro-sulphates of M. Pelouze. I found, on varying the

proportions of sulphurous and nitrous acids, different salts might be obtained, which were all remarkable for their stability and their beautiful crystalline forms. It is my intention to continue these researches as soon as I have terminated those on osmium.—*Comptes Rendus*, June 10, 1844.

Observations on Oxide of Phosphorus.

When, according to Berzelius, a large surface of phosphorus is exposed for some time to a dry atmosphere, in which the absorbed oxygen can be gradually replaced, it slowly oxidizes at the expense of the air, but without fuming and forming phosphorous acid as in moist air. In this operation it is converted into a brown mass, which is the phosphate of the oxide of phosphorus, and which is decomposed by water. This compound is obtained more quickly and in larger quantity by pouring liquid sulphuret of phosphorus into a flask containing dry air, and which is closed with a cork, and allows of a change of air, by means of a short chloride of calcium tube, to prevent any moisture from entering. The interior of the flask soon becomes coated with a brown tenacious mass, which gradually increases. At the end of a week the flask is filled with water, in which the brown mass dissolves to a beautiful yellow milk; this is removed with a siphon to prevent any of the undecomposed sulphuret of phosphorus accompanying it. The liquid is then heated to 176° Fahr., when it becomes clear, with deposition of a beautiful yellow hydrate of the oxide of phosphorus, which contains no sulphur. It should be washed and dried in the air.—*Jahresbericht*, xxiii. p. 43.

On the Action of Ammonia on Butyric Æther. *By* M. G. Chancel.

Butyric acid may now be obtained in sufficient quantity by the fermentation of sugar, for the purpose of submitting the different combinations to which it gives rise to more accurate investigation.

The author was induced to examine the action of some agents on butyric æther, the formation of which is so precise and easy. We know that oxalic æther, under the influence of caustic ammonia, produces oxamide, a substance discovered by M. Dumas, who described it as the type of a series of combinations, designated by the generic name of *amides*. It was probable that butyric æther would undergo a similar reaction; the experiment has wholly confirmed this supposition. The action of caustic ammonia on butyric æther takes place, it is true, but slowly and with difficulty, but it is complete, and gives rise to a substance which crystallizes with facility, and which possesses all the characters of an *amide*.

Butyramide.

When liquid ammonia and butyric æther are mixed, the liquid is at first rendered turbid and milky, but the æther speedily separates on the surface. Nevertheless, at the ordinary temperature, by taking care to agitate the two liquids frequently, the butyric æther

is decomposed, the layer diminishes from day to day, and after a sufficient lapse of time it ends by disappearing entirely. By introducing 1 part of butyric æther and from 5 to 6 parts of ammonia into a well-stoppered flask, the action, being assisted by frequent agitations, is complete after eight or ten days; on evaporating the liquid to the third of its primitive volume, the butyramide crystallizes on the cooling of the liquor. This substance therefore is produced under similar circumstances as *oxamide* and *succinamide*, which has been recently discovered by M. Fehling.

Butyramide crystallizes in brilliant white prisms of a mother-of-pearl lustre; it is colourless, transparent, undergoes no alteration by contact with air, and possesses a sweet and cool flavour, which is succeeded by a bitter taste. It melts at a temperature of about 239° Fahr. into a colourless liquid, which volatilizes slowly when kept in fusion; the vapours are inflammable; it is moreover volatile, without residue; it is easily soluble in water, more considerably so in hot than in cold water; it is equally soluble in alcohol and in æther. Thrown upon water, it dissolves without producing those gyratory movements common to several soluble butyrates; under the influence of a boiling temperature, the aqueous solution of butyramide is decomposed by alkalies into ammonia and butyric acid; thus, by adding some hydrate of potash to a solution of butyramide in water, no appreciable disengagement of ammonia is observed when cold, but a great quantity by ebullition. The author has not yet submitted the butyramide to the action of any other agent.

The analysis of this substance has furnished results which lead precisely to the following formula:—

$$C^8 H^9 N O^2 = C^8 H^7 O^2, NH^2.$$

The equivalent of butyramide is represented therefore by the number 1089·54.

This composition confirms the formula for butyric acid advanced by MM. Pelouze and Gelis.

The formation of butyramide under the circumstances just mentioned is expressed by the following equation:—

$$\underbrace{C^4 H^5 O, C^8 H^7 O^3}_{\text{Butyric æther.}} + \underbrace{NH^3}_{\text{Ammonia.}} = \underbrace{C^8 H^7 O^2, NH^2}_{\text{Butyramide.}} + \underbrace{C^4 H^5 O, HO}_{\text{Alcohol.}}.$$

The author proposes to examine the action of dry ammonia on butyric æther, as well as the other products of decomposition, to which different agents may give rise.—*Comptes Rendus*, May 20, 1844.

Analysis of the Ashes of Potatoes.

These consist, according to M. Vogel, of 17·5 per cent. insoluble and 82·5 soluble salts. The former consist of 9 per cent. phosphate of lime with some phosphate of magnesia, alumina and peroxide of iron, and of 8·5 per cent. carbonate of lime, with some carbonate of magnesia; there is no silica present. The latter consist principally of alkaline carbonates, sulphates and phosphates (5·33 phosphates, 6·93

sulphates), and traces of metallic chlorides. The soda constantly amounts to 1 per cent. more than the potash.—*Ann. de Chem. et Pharm.*, xlix. p. 245.

On the Carbonates of Copper. By M. Favre.

As is well known, the carbonates of copper dissolve in sesquicarbonate of ammonia, forming a solution of a beautiful blue colour, but the nature of the compound produced was hitherto unknown. M. Favre having obtained this compound well-crystallized, analysed it, and investigated the changes which it undergoes. To prepare it he adds to a blue concentrated and saturated solution of carbonate of copper in carbonate of ammonia, twice its volume of alcohol; after twelve hours the sides of the vessel are covered with large and beautiful crystals of a very deep blue colour, analogous to that of the native carbonate from Chessy. The composition of these crystals is expressed by the formula CuO, NH^3, CO^2. Water decomposes them rapidly, an aqueous solution of carbonate of ammonia dissolves them entirely, but alcohol has no action on them, and may be employed for washing them.

This salt may likewise be obtained by digesting carbonate of copper and carbonate of ammonia in alcohol, or by mixing the dry copper and ammoniacal salts, and exposing the mixture to a temperature of 212°, when it fuses, gives off its water and the excess of ammoniacal salt, and then solidifies with a beautiful intense blue colour. If the salt is heated to 392° in a current of carbonic acid, anhydrous carbonate of ammonia sublimes, and a portion of the oxide of copper is reduced. Exposed quickly to a higher temperature, it is decomposed with a very lively deflagration; and if the experiment is made in a current of carbonic acid, the residue is metallic copper.

The liquid from which the crystals had been deposited, exposed to the air, formed a bluish-green crystalline crust, a carbonate which is represented by the formula $2CuO, CO^2, 2HO$. When dried by exposure to the air, it is able to bear heating to 194° without losing an equivalent of water; whilst when heated in presence of water, that temperature quite suffices to deprive it of this equivalent.

Lastly, if the same blue liquid from which the first crystals of ammoniacal carbonate of copper were deposited is diluted with a large quantity of water, a salt is precipitated, which is blue at the moment of its formation, and when simply dried in the air at a temperature of 122° to 140°, but which, when dried at 230°, loses the equivalent of water, assumes the green tint of the acetate of copper, and is composed according to the formula $3CuO, CO^2 + 2HO$. This salt has the same formula as the native carbonate of Chessy, viz.

$$3CuO\ 2CO^2\ HO$$
$$3CuO\ 2HO\ CO^2,$$

the water replacing the carbonic acid, and *vice versâ*.

The author next investigated the influence of heat on the hydrate and on the carbonates of copper, and ascertained in this manner that the presence of water lowers the point of decomposition of the salts, and that the liberation of the water is always accompanied by that of carbonic acid.

From this observation he concludes that water and carbonic acid differ but slightly in their degree of affinity in presence of oxide of copper, and that the multiplicity of carbonates of copper is very readily explained from the feeble affinities of their constituent elements.—*Journ. de Pharm.* for April 1844.

On Maynas Resin. By M. Lewy.

This resin, which is principally derived from the province of Maynas in America, whence its name, is furnished by the *Callophyllum Calaba.* The resin is extracted by incision; in the recent state it is white and limpid, but it becomes thick by exposure to the air, and acquires a yellowish colour. It resembles in its external characters most of the resins; but on purifying it by solution in boiling alcohol, it separates in the form of small transparent prisms. When the crystallization is effected slowly, very beautiful crystals, of a fine yellow colour and of considerable size, are obtained. According to M. Provostaye, they form oblique rectangular prisms.

On analysis the purified resin afforded the following results:—

Carbon	67·22	67·59	= 14	1050·0	67·20
Hydrogen	7·31	7·25	= 9	112·5	7·20
Oxygen	25·47	25·16	= 4	400·0	25·60
				1562·5	

This formula would represent benzoic acid + 3 equivalents of hydrogen.

I endeavoured to determine the equivalent of this substance by forming a silver salt, but six different preparations did not afford constant results. The salt is obtained by dissolving the resin in caustic ammonia, expelling the excess of ammonia, and precipitating the clear solution with neutral nitrate of silver.

This resin behaves like an acid; it enters into combination with bases, dissolves readily in potash, soda and ammonia, even without the assistance of heat; it is insoluble in water, very soluble in alcohol, æther, and in the essential and fatty oils. Its density is 1·12; it melts at about 221° Fahr. to a transparent liquid, in which state it continues for some time, and does not solidify till about 194°. Submitted to dry distillation, it affords empyreumatic oils and a carbonaceous residue. It dissolves in cold acetic acid, and likewise in sulphuric acid; the latter acquires a beautiful red colour, but water throws down the resin unaltered. On heating it with a mixture of bichromate of potash and sulphuric acid, it gives off carbonic acid, and at the same time formic acid is generated. Fuming nitric acid has a very lively action on it; a yellowish-white nitrogenous acid is obtained on precipitation with water, which is incrystallizable and

soluble in alcohol and æther. It was not obtained of constant composition. When digested with nitric acid of 1·31 spec. grav., it disengages abundant red vapours, and a liquid and volatile acid is formed, which possesses all the characters of butyric acid. A liquid remains in the retort, which on concentration affords small crystals of oxalic acid. A crystalline acid, soluble in water, which does not precipitate salts of lime, is also obtained; but the small quantity of material at my disposal prevented further examination.—*Ann. de Chim. et de Phys.*, March 1844.

ANALYTICAL CHEMISTRY.

An Account of some new Instruments and Processes for the Analysis of the Carbonates. By Profs. William B. Rogers and Robert E. Rogers, of the University of Virginia.

Induced by the recent researches and impressive suggestions of Dumas, in relation to the equivalents of oxygen, carbon and calcium, we several months ago entered upon a series of investigations, to test for ourselves the accuracy of the received atomic weights of lime, magnesia, baryta, strontia, soda and potash, proposing, as the simplest means of effecting this object, to determine the amount of carbonic acid evolved from the pure carbonates by some process similar in principle to that above described. Repeated trials, however, convinced us that the imperfections incident to Rose's process and others that have been recently proposed, though of but little moment in ordinary analysis, unfitted them for the higher description of research. A more critical examination of the sources of irregularity and error in these and the other methods of analysis, at length led us to the forms of apparatus and modes of procedure which we have since employed with very satisfactory results.

These instruments and manipulations we will now proceed to sketch, accompanying the description with a reference to some of the experiments used as tests of the accuracy of our process, or as proofs of the errors not hitherto adverted to in the methods commonly in use.

The main apparatus, that in which the decomposition is effected, and which is weighed at the beginning and close of the process, is of two distinct forms, adapted to the different characters of the carbonates under examination. Of these, one is seen forming the middle portion of fig. 1, the other is delineated in fig. 2.

The body of the instrument in both cases consists of a light wide-mouthed bottle, having a capacity of about 3 cubic inches, closed by a cork three-fourths of an inch in thickness. In *the first form*, the cork receives the tapering ends of two drying tubes, the one horizontal, the other vertical, both projecting a short distance into the bottle. It is also penetrated centrally by a stout platinum wire about 4 inches long, hooked at the lower and bent twice at the

Fig. I.

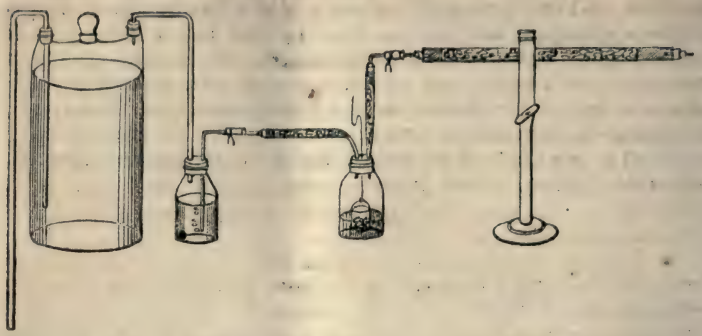

Fig. II.

upper end. A thin glass bucket for containing the solid carbonate is represented in the figure as hanging within the bottle. This is perforated at the bottom, and furnished with a handle of platinum wire, to allow of its suspension from the upper and from the lower hook in the successive stages of manipulation. Such is the arrangement we employ in experiments with carbonates of lime, baryta and soda, and the other carbonates which admit of accurate weighing while exposed.

In the second form, the platinum wire and glass bucket are omitted; the carbonate, inclosed in a thin sealed tube, is placed at the bottom of the bottle, and the hydrochloric acid retained until needed in the globular pipette above. The latter appendage, drawn out to a delicate and even tube below, is inserted through the centre of the cork, and projects into the bottle about three-fourths of an inch. As in this arrangement the column of acid is exposed to an undiminished atmospheric pressure at top, some care is necessary in forming the tapering stem of the pipette, otherwise the liquid will escape in drops during the first weighing. This is obviated by a very *gentle* convergence of the tube, and by drawing in a column of air, so as to fill the lower half or two-thirds of its length. With these precautions, we have found the acid to be retained in the bulb, without the slightest tendency to drop. The drying tubes belonging to this form are both bent horizontally, and inserted, the one through the cork of the bottle, the other through that of the pipette. This form of the instrument we use for such carbonates as are very hygrometric, and could not therefore be weighed in the bucket, and also for such as are very bulky, as those of magnesia and zinc. We have moreover found it more convenient than the other, where the compound formed by the reaction is insoluble and forms a pasty mass, as when sulphuric acid is employed to decompose carbonate of lime.

In both forms of the apparatus, the outside of the bottle, pipette

and drying tubes should be well coated with a smooth varnish of shell-lac, and the corks, and especially that of the bottle, should be repeatedly coated and dried, so as to be well imbued with the varnish for some depth. This is so important a precaution, that unless the large cork happen to be uncommonly close in texture, the permeation through it, in experiments of long continuance, is capable of producing very serious errors.

To the parts here described, which in both forms compose the apparatus proper, certain appendages are added in the course of the experiment. These, as shown in fig. 1, to the left and right of the decomposing bottle, are as follows:—

1. *A large drying tube*, 10 inches long, filled for an inch at each end with dry cotton, and throughout the intervening 8 inches, with chloride of calcium properly desiccated. This, supported in a horizontal position, is connected by a gum-elastic tube with the little supplemental bent portion of the upright drying tube. It is made thus long to ensure the absence of moisture in the air drawn into the apparatus in the process of aspiration.

2. *An arrangement for aspiration*, consisting of a three-necked Wolfe's bottle, holding about 50 cubic inches, to which are adapted a long glass siphon on the one side, a bent connecting tube on the other, and a ground stopper in the middle aperture. The bottle being filled with water, the siphon is made to operate by applying the lips below, and a stream of dry air is drawn into and through the apparatus as long as the water continues to flow. A short tube, drawn to a small orifice, and made to fit over the end of the siphon, or what is better a small stopcock, may be used to regulate the stream.

3. *A test bottle*, containing a solution of nitrate of silver, placed between the decomposing vessel and the instrument for aspiration. This appendage is introduced in the figure and referred to here, not because we deem it essential when the operation is conducted with even common care, but as necessary to complete the picture of the apparatus of research as used by us in our experiments. It will be shown hereafter, contrary to the intimation of Erdmann and Marchand, that hydrochloric acid *does not* pass through the drying tubes, either in company with the stream of evolved carbonic acid, or during the aspiration with the air. As however an extreme violence in the effervescence, accidentally occasioned, *might* cause some of it to escape, a fact not yet witnessed in any of our experiments, we continue to use this appendage as a sentinel to give us notice of the error.

In adjusting the apparatus for use, great care should be taken to make all the connexions, from the remote end of the large drying tube to the short tube of the test bottle inclusive, perfectly *air-tight*.

We will now briefly sketch our mode of using the apparatus in exact research, and describe a further process which we have found necessary for expelling the carbonic acid from the liquid.

When the bucket is used, a small bit of tissue paper is pressed down upon its bottom, so as completely to close the aperture, and then

the weighed carbonate, usually 100 grs., is carefully transferred into it. Having charged the bottle with moderately dilute hydrochloric or sulphuric acid, in quantity a good deal more than is required to neutralize the carbonate, and having properly adjusted the cork, we hang the bucket with its contents upon the upper hook of the platinum wire, and lifting the apparatus carefully into the scale, we counterpoise it with great care; then withdrawing it from the scale, we lift off the bucket, remove the cork, attach the bucket to the *lower hook*, previously drawn up so as nearly to touch the lower side of the cork, and again secure the cork in its place. As it now hangs, the bucket is from one-half to three-fourths of an inch above the level of the liquid. Depressing the wire, we plunge the bucket into the fluid, which enters by the aperture below, and varying the depth of immersion from time to time, we regulate the effervescence so as to be uniformly brisk, but without great violence.

The effervescence having ended, as shown by the absence of any crepitation when the ear is held close to the flask, the liquid is briskly agitated to favour the escape of adhering bubbles, and the instrument is now connected with the appendages above described, in the manner indicated in fig. 1. The siphon being set in action, and the closeness of the connexion ascertained, as before directed, the aspiration is commenced. During this process, which occupies from 15 to 20 minutes, drawing through the apparatus 50 cubic inches of dry air, the bottle is several times gently shaken from side to side, to promote the escape of the combined carbonic acid from the liquid. The instrument is now withdrawn from the appendages, and again placed on the scale to be weighed. In this second weighing it will sometimes happen that the apparatus loses while on the scale a small amount of weight, rarely however exceeding a few thousandths of a grain, arising, as we have clearly proved, from the gradual escape of more of the combined carbonic acid from the liquid. In such cases we repeat the process of aspiration, after which the weight remains without sensible diminution during the weighing.

In using the pipette form of apparatus for the deliquescent carbonates, the substance to be examined is placed in a thin glass tube, previously weighed. The tube is then drawn out nearly to a point by the use of a weighed fragment of a glass rod over an alcohol lamp. Sufficient heat being applied thoroughly to dry the carbonate, the fine end of the tube is closed, and the whole suffered to cool down to the surrounding temperature. The point of the tube is then removed with a sharp file, to allow air to enter, after which it is closed by the application of a small stopper of wax-cement of known weight. In this condition the tube, together with the little piece removed from its point, and the fragment of rod, are placed in the scale and counterpoised. The entire weight, thus obtained, diminished by the sum of the weights of the tube, rod and stopper, gives the weight of the dry carbonate in the tube.

The pipette being charged with acid and adjusted so as not to produce drops, the tube is allowed to fall into the bottle with such force as to be broken, and the cork is instantly secured in its place.

To inject the acid into the bottle, we attach the *large drying tube* to the upper drying tube of the instrument, and then operate either by suction with the mouth applied to a little mouth-piece at the other end of the apparatus, or by connecting it with the appendage for aspiration.

The weight of the carbonic acid employed being then accurately determined, the process has reached the stage at which it has heretofore been regarded as terminated; but numerous observations have proved to us that, even after two protracted aspirations, the amount of carbonic acid retained by the liquid is far too considerable to be overlooked, and that to effect its complete separation it is necessary to boil the liquid.

To separate and measure this portion of the carbonic acid, we employ a tube of thin glass about 24 inches long and one-fourth of an inch in calibre, closed at one end, and graduated at this extremity to fiftieths of a cubic inch. Pouring mercury into this until the vacant space above is not much more than sufficient to contain all the liquid in the bottle, we pour the liquid upon the mercury, holding the tube in an inclined position, so as to produce as little agitation as possible, and then add mercury until the tube is completely filled. Inverting the instrument in a bowl of mercury and supporting it in an inclined position, we apply the flame of a spirit-lamp to the part containing the acid solution. But little carbonic acid is evolved until near the boiling point. The bubbles then rapidly ascend, and the gas continues to be disengaged even after the commencement of ebullition, so that to ensure its entire separation this temperature should be maintained for two or three minutes. The tube, placed in an erect position, may now be brought to the temperature of the apartment by a moist cloth.

A saturated solution of common salt being poured upon the mercury in the bowl, the tube is to be raised a little, so as to permit this liquid to ascend and take the place of the mercury in the tube, after which the instrument is transferred to a deep narrow jar, filled also with the saturated solution, and is depressed to the proper level for measuring the volume of the included gas. As this volume always includes a minute quantity of common air, disengaged from the liquid by boiling, the tube must now be transferred to a large cistern of water, when, by continued agitation for a minute or two, all the carbonic acid will be absorbed, and thus its volume made known by subtraction. These processes being conducted at or near the temperature of the room, or the volume being corrected for expansion, should the temperature be much higher, the height of the residuary carbonic acid is given with sufficient accuracy by estimating each tenth of a cubic inch as equivalent to 0·047 gr.

This supplemental process, though seemingly tedious and troublesome, is readily completed in from fifteen to twenty minutes, and *ought never to be omitted* when great accuracy is in view. As proving its importance, we may state that in the great number of experiments which we have made within the last few months by the method above described, we have found the amount of absorbed

carbonic acid to be rarely less than one-twentieth, and sometimes as much as one-fifteenth of a cubic inch; *varying thus from one-twentieth to one-fifth of a per cent. of the whole weight of that substance contained in the carbonate employed.*

That the carbonic acid, thus united with the liquid, cannot be expelled by Rose's method, is apparent from the fact that its removal can only be effected by an actual boiling of the liquid; and this, if attempted in the flask, would lead to far more serious errors than that proposed to be corrected. In proof of the latter statement, we would refer to the following experiments:—

1. Having prepared a solution with carbonate of lime and the usual charge of dilute hydrochloric acid, and boiled it to expel the dissolved carbonic acid, we introduced it into a small bottle furnished with an ample drying tube, the junctions being all secured air-tight. After careful counterpoising at 64°, we heated it gradually over a small lamp until it began to boil briskly. On withdrawing it from the lamp, the chloride of calcium was found to have been moistened by the condensed steam for about half the length of the tube. The original temperature restored, the instrument was placed in the scale. It had lost five-tenths of a grain.

2. Supposing that this loss might be due to the escape of hydrochloric acid, we made a similar trial with sulphuric acid, and found the reduction of weight to be about six-tenths of a grain.

3. Still further to assure ourselves that the hydrochloric acid had not escaped in the former experiment, we renewed the charge, and while heating the liquid passed the vapour and air, as they escaped from the drying tube, through a solution of nitrate of silver in a test glass. No impression was made upon the test solution up to the period at which the former experiment was discontinued; but as soon as the whole length of the drying tube was moistened by condensed vapour, the escape of hydrochloric acid was indicated by dense curds of the precipitated chloride. A like trial with the sulphuric solution gave, even *earlier*, the same result, the sulphuric acid carried over with the steam decomposing the chloride of calcium and liberating hydrochloric acid.

It is evident, therefore, that the application to Rose's apparatus of a heat sufficient to expel the carbonic acid from the solution is entirely inadmissible, whichever solvent we employ. It is scarcely necessary to add, that this remark is also applicable to the apparatus of Fritzsche, that of Will and Fresenius, and that of Erdmann and Marchand.

As in a recent memoir of the two chemists last named, they express a preference for *sulphuric acid* in experiments of this kind, it became important to our inquiries to ascertain whether the sulphuric solution produced in such case would retain enough carbonic acid to make the boiling process necessary. We therefore introduced into the bottle 100 grs. of carbonate of lime, and poured upon it a sufficient amount of sulphuric acid, diluted with an equal bulk of water, to prevent the formation of a thick magma. Notwithstanding the large excess of acid and frequent agitations of the liquid, the action towards its close was extremely slow, so that at the end of

four hours a slight crepitation could be heard on stirring the mixture. When this had entirely ceased, the liquid was heated in the graduated tube as above described. As the temperature approached boiling, carbonic acid was evolved, and at the close of the process the volume of this gas collected was upwards of four-tenths of a cubic inch. A similar result was obtained with several other carbonates and sulphuric acid.

We are therefore justified in affirming, that the solution or mixture formed in this process, whether sulphuric or hydrochloric acid be used, always contains an amount of carbonic acid too great to be overlooked in accurate research; that this carbonic acid cannot be expelled by a heat below boiling, and that such a temperature cannot be applied to the liquid *while in the apparatus* without entirely vitiating the result.—Silliman's *Journal* for April 1844.

Test for Arsenic.

Dr. Baumann recommends, for detecting small quantities of arsenic, triturating the suspected body with from 3 to 6 times its volume of iron-filings, which have been exposed to a red heat, and are known to be free from arsenic, and heating the mixture on charcoal in the reducing-flame of the blowpipe. Even with the smallest quantity of arsenic, the odour at least is disengaged.—*Archiv der Pharm.*, xxxv. p. 264.

CHEMICAL PREPARATIONS.

On the Preparation of Chlorine Water, and on the Determination of its Amount of Chlorine. By M. A. Buchner, Sen.

Numerous complaints having recently been made respecting the unequal nature of this preparation, which at the present time is coming into considerable use, the author was induced to communicate his experience respecting this preparation, from which we extract the following:—

Comparison of the Formulæ of different Pharmacopœias.

According to the *Bavarian Pharmacopœia*, 4 parts of salt are taken to 1 of manganese, and the chlorine disengaged from it with 2 parts concentrated sulphuric acid which has been diluted with 6 parts water; the gas is conducted into Woulf's bottles containing 40 parts water. It is easily shown by calculation, that, according to this formula, too little manganese and sulphuric acid is taken to decompose the whole of the salt, and at the same time to prevent hydrochloric acid passing over, and so contaminating the product. This formula appears to be a modification of that of the Paris Codex of 1818, which ordered 250 manganese, 1000 concentrated sulphuric acid, diluted with 500 water, 1000 salt, and 40000 parts of water to absorb the chlorine gas.

We find the same bad proportion of 1 part manganese to 4 parts

salt likewise in the *Austrian Pharmacopœia* of 1834, the sulphuric acid however calculated for 6 parts. It also directs the chlorine to be passed through cold water, distributed in several Woulf's bottles, and to throw away the contents of the first bottle at the end of the operation, so as to ensure the chlorine water being free from muriatic acid.

The *Prussian Pharmacopœia* directs the chlorine gas (liberated from a mixture of 3 parts salt, 1 manganese, 2 concentrated sulphuric acid, 2 water at a gentle heat) to be passed into bottles filled with cold distilled water, and reversed in a pneumatic trough, so that two-thirds of the water in volume are expelled by the gas, and only one-third water is left, which is then saturated with the chlorine gas by shaking the closed and inverted bottle. In this prescription, in which the quantitative proportion of the ingredients is somewhat better determined, it is supposed that 1 volume of cold water is capable of absorbing 2 volumes of chlorine, which is perfectly correct. This method affords the twofold advantage, that on following it carefully a constantly equal and perfectly saturated water is obtained, which cannot be contaminated with muriatic acid, presupposing that during and after the operation the influence of sunlight has been guarded against as much as possible. It is however open to this objection, that the proportion of the manganese to the salt is likewise too small.

For this reason Pfaff has ordered, in the *Pharmacopœia of Schleswig-Holstein*, 3 parts manganese, 5 parts concentrated sulphuric acid diluted with 5 parts water to 6 parts salt; we have therefore $1\frac{1}{2}$ manganese and $2\frac{1}{2}$ sulphuric acid to 3 of salt.

The *Hanoverian Pharmacopœia* orders 16 oz. of salt, 16 of manganese, and 24 of sulphuric acid with 12 of water; we have therefore 3 parts manganese and $4\frac{1}{2}$ sulphuric acid to 3 of salt, and are certain of obtaining the whole of the chlorine.

The authors of the *Danish Pharmacopœia*, in the edition for 1840, have calculated the proportion of salt and manganese at equal equivalents, and have ordered the chlorine gas to be expelled from 12 parts salt by 9 of manganese and 20 of sulphuric acid which has been diluted with its equal weight of water, and the gas to be absorbed by one-third volume of water, in the same manner as directed in the Prussian Pharmacopœia.

In the *Pharmacopœia of Baden* we again find a smaller proportion of manganese, viz. only 2 parts to 3 of salt, and on the other hand 5 parts of concentrated sulphuric acid diluted with $2\frac{1}{2}$ water. The chlorine gas is likewise combined, according to the *Pharm. Boruss.*, by shaking with one-third volume of water.

The *Pharmacopœia Universalis* contains two distinct formulæ. According to the one, the chlorine is liberated from 4 oz. of salt by 3 of manganese (therefore in equal equivalents), and 8 of concentrated sulphuric acid diluted with 4 of water; it is passed into three or four Woulf's bottles, the first of which is smaller and contains some solution of potash, to retain the muriatic acid which passes over; 16 lbs., *i. e.* 192 oz. of cold distilled water, are distributed between

the two or three flasks to absorb the purified chlorine. Since the manganese, as usually employed, is not pure peroxide, 3 parts are somewhat too little to 4 parts of salt. According to the second formula, the gas is liberated from 4 oz. of muriatic acid by 1 of manganese, and absorbed, according to the method of the *Pharm. Boruss.*, by one-third volume water.

On comparing these different formulæ, we find that an equally good and saturated water can be prepared from each of them if attention be paid to the temperature of the water; if, further, care be taken that an excess of chlorine is liberated to saturate the water entirely, and if the absorption is allowed to proceed in such a manner that a contamination of the product with muriatic acid be prevented; and lastly, if the influence of the sun's light, and all other agents which might exert a decomposing action on the water, be carefully avoided. It is absolutely necessary that the chlorine water be preserved, in a dark situation, in glass bottles provided with ground-glass stoppers.

The author has convinced himself that the chlorine gas is obtained, without any washing, perfectly free from muriatic acid, if the mixture be not too strongly heated and a sufficient excess of manganese be employed. He disengages his chlorine from 1 part manganese, 3 of crude muriatic acid of 1·130*, and 1 water, and absorbs it in 28 parts water, in which operation the chlorine is passed as slowly as possible through the water, and the whole process conducted in a black-coated bottle or in a dark place. If we admit that 1 vol. water absorbs on an average 2 vol. chlorine (therefore 1000 parts by weight of water, 6·34 parts by weight of chlorine), 55 parts of water might be saturated with the chlorine evolved from the 3 parts muriatic acid of 1·130. As however the ingredients are by no means expensive, Buchner prefers wasting a little, to be certain that the chlorine water is at all times saturated, since the chlorine gas is neither so easily nor so rapidly condensed by water as hydrochloric acid. Moreover, every waste may readily be avoided, by passing the excess of chlorine into hydrate of lime, so as not to be troubled with the odour of chlorine, and at the same time chloride of lime is obtained as a secondary product.

It was proved, by an experiment made on purpose, that an excess of chlorine was necessary in order to obtain, under ordinary circumstances, a well-saturated water; for taking only 6 oz. of muriatic acid and 2 oz. of manganese to 112 of water, a proportion which, according to calculation, is far more than suffices to produce a perfectly saturated chlorine water, yet, notwithstanding all care and attention, this chlorine water bore no comparison to that prepared according to the above proportion; it was paler, and indicated, on a comparative examination, a smaller amount of chlorine than there ought to have been according to calculation.

* The same proportion is prescribed by the *Cod. Medic. Hamburg*, in which however the chlorine is absorbed by its equal volume of water. The new French Codex prescribes 4 parts muriatic acid to 1 of manganese, but the latter is then supposed to be perfectly pure.

Amount of Chlorine in Chlorine Water.—According to Pelouze, 1 vol. water can absorb, according to the temperature, from 0·6 (at 158°) to 2·7 (at 50°) vol. chlorine*. Detmar found at 59°, 2 vol. or 6·63 grms. chlorine to 1000 grms. water; this would give for each ounce 3 grs. of chlorine, which however is never attained, as much is lost on pouring the chlorine water into other vessels. We can at the most suppose, in the chlorine water which is dispensed, 2·5 grs. of chlorine per ounce on an average.

[To be continued.]

Hair-Dye.

M. Wimmer strongly recommends pyrogallic acid for colouring gray hair permanently brown. It is best to employ the acid which has been prepared by sublimation from galls in Mohr's apparatus, dissolved in water, separated from empyreumatic oil, treated with animal charcoal, then concentrated, and alcohol added to it; the disagreeable odour is disguised by an essential oil. Care must be taken, on applying the tincture, not to touch the hands or other parts of the flesh with it, as the colour is extremely difficult to remove.—Buchn. *Repert.*, xxxiii. p. 88.

On the Preparation and Therapeutic Employment of Valerianate of Zinc. By MM. Muratori and Cerutti.

This new remedy is much employed in Italy in nervous diseases, and appears to be a remedy of sure efficacy in that class of cases, and a valuable addition to our means of treating them. Its formation is not difficult, if we have previously obtained its two elements in a state of purity. Let a quantity of hydrated protoxide of zinc, sufficient to saturate the acid, be gradually added to a quantity of valerianic acid. Heat favours the combination. Then pour the solution of the salt into a porcelain vessel, adding a small quantity of protoxide of zinc to neutralize any uncombined acid, concentrate the solution by evaporation, and a white crust of valerianate of zinc will form on the surface, which is to be removed as it forms, and after being dried put into a close phial. M. Muratori has also obtained the salt by the double decomposition of sulphate of zinc and valerianate of lime; a solution of valerianate of zinc is thus obtained, sulphate of lime being thrown down. The fluid is then concentrated. M. Cerutti effected a cure in three cases of supra- and infra-orbital neuralgia, by giving it in doses of $1\frac{1}{2}$ gr. daily, divided into two pills, and taken at the moment of accession of the paroxysm. In one case the cure was complete in thirty days, in forty in another, and in fifty in the third.—*Gaz. Med.* and *Ed. Month. Journ.* for June 1844.

* The absorption diminishes below 50°; it is therefore quite improper to cool the water artificially in the preparation of chlorine water, leaving out of question the formation of hydrate of chlorine.

PROCEEDINGS OF SOCIETIES.

Meeting of the Royal Institution.

Friday, June 7, 1844.

MR. FARADAY "On recent Improvements in the Manufacture and Silvering of Mirrors."

Mr. Faraday's subjects were,—1, the manufacture of plate glass; 2, the *ordinary* mode of silvering mirrors; 3, the *new* method of producing this result, lately invented and patented by Mr. Drayton.

1. Mirrors are made with plate glass. Mr. Faraday described glass generally as being essentially a combination of silica with an alkaline oxide. The combination however presents the character of a solution rather than of a definite chemical compound; only it is difficult to affirm whether it is the silica or the oxide which is the solvent or the body dissolved. From this mutual condition of the ingredients, it follows that their product is held together by very feeble affinities; and hence, as was afterwards shown, chemical reagents will act upon these ingredients with a power which they would not have were glass a definite compound. Mr. Faraday noticed, that as glass is not the result of definite proportionals, there are many combinations of materials capable of producing a more or less perfect result. Each manufacturer therefore has his own recipe and process, which he considers the most valuable secret of his trade. It is, however, well known that the flint glass maker uses the oxides of lead and of sodium, the bottle glass maker lime (an oxide of calcium), and the plate glass maker, in addition to soda, has recourse to arsenic. Mr. Faraday then adverted to the corrosions which take place in the inferior qualities of glass, owing to the feeble affinity with which their ingredients are held together. He stated, that from the surface of flint glass a very thin film of soluble alkali was washed off by the first contact of liquid, leaving a fine lamina of silica, the hard insoluble quality of which protected the substance which it covered. If however this crust of silica chanced to be mechanically removed, the whole of the glass became liable to corrosion, as in ancient lachrymatories and other glass vessels. Mr. Faraday illustrated this by the corroded surfaces of two bottles, one obtained from a cellar in Threadneedle Street, where it had probably remained from the period of the great fire of London, another from the wreck of the Royal George. A still more striking instance of the instability of glass as a compound was exhibited by formations in the interior of a champagne bottle, which had been filled with diluted sulphuric acid. In this case the acid had separated the silica from the inner surface of the glass, and formed a sulphate with the ingredient, lime. The result was, that the bottle became incrusted internally with cones of silica and sulphate of lime, the bases of which, extending from within outwards, had perforated the sides of the bottle so as to cause the escape of the liquor it contained. Mr. Faraday referred to the long period of annealing which glass had to undergo as a necessary consequence of glass wanting

the fixity of a definite compound. He concluded this part of his subject by describing the mode of casting plates, and the successive processes which gradually produce the perfect polish of their surface.

2. Mr. Faraday next exhibited to the audience the mode of silvering glass plates as commonly practised. He bade them observe that a surface of tinfoil was first bathed with mercury, and then flooded with it; that on this tinfoil the plate of glass, having been previously cleansed with extreme care, was so floated as to exclude all dust or dirt; that this was accomplished by the intervention of $\frac{1}{8}$ in. of mercury (afterwards pressed out by heavy weights) between the reflecting surface of the amalgam of the mercury and the glass; and that when the glass and amalgam were closely brought together by the exclusion of the intervening fluid metal, the operation was completed.

3. The great subject of the evening was the invention of Mr. Drayton, which entirely dispenses with the mercury and the tin. By that gentleman's process the mirror is, for the first time, literally speaking, *silvered*, inasmuch as silver is precipitated on it from its nitrate in the form of a brilliant lamina. The process is this:—On a plate of glass, surrounded with an edge of putty, is poured a solution of nitrate of silver in water and spirit, mixed with ammonia and the oils of cassia and of cloves. These oils precipitate the metal in somewhat the same manner as vegetable fibre does in the case of marking ink, the quantity of oil influencing the rapidity of the precipitation. Mr. Faraday here referred to Dr. Wollaston's method of precipitating the phosphate of ammonia and magnesia on the surface of a vessel containing its solution, in order to make intelligible how the deposit of silver was determined on the surface of clean glass, not (as in Dr. Wollaston's experiment) by mechanical causes, but by a sort of electric affinity. This part of Mr. Faraday's discourse was illustrated by three highly striking adaptations of Mr. Drayton's process. He first silvered a glass plate, the surface of which was cut in a ray-like pattern; 2nd, a bottle was filled with Mr. Drayton's transparent solution, which afterwards exhibited a cylindrical reflecting surface; and 3rd, a large cell, made of two glass plates, was placed erect on the table, and filled with the same clear solution. This, though perfectly translucent in the first instance, gradually became opake and reflecting; so that, before Mr. Faraday concluded, those of his auditors who were placed within view of it saw their own faces, or those of their near neighbours, gradually substituted for the faces of those who were seated opposite to them.—*Athenæum.*

THE CHEMICAL GAZETTE.

No. XLII.—July 15, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Iodic Acid and its Salts. By M. Millon.

Preparation of Iodic Acid.—After a careful comparative examination of the various methods in use, the author has adopted the following:—First of all, it is necessary to procure *pure* iodine, for even iodine which is entirely volatile and soluble in alcohol always contains a tolerable quantity of iron, which is only imperfectly removed by boiling it with dilute muriatic or nitric acid; the iron, however, is wholly separated by passing a current of sulphuretted hydrogen gas through iodine suspended in 15 to 20 times its weight of water. The purest iodine is obtained by treating a solution of iodide of potassium with chlorine gas until the separated iodine is redissolved, and then pouring the solution into another solution of iodide of potassium, containing at least three times as much of the iodide. The iodine is precipitated, and requires only to be filtered, washed and dried. 80 grs. of pure iodine are now boiled in a flask with 75 grs. chlorate of potash, 400 grs. water and 1 gr. nitric acid, until a lively evolution of chlorine ensues; it is then removed from the fire, and if the iodine has entirely disappeared (*i. e.* transformed into iodic acid), it is treated with a solution of 90 grs. nitrate of barytes; the iodate of barytes is washed two or three times by decantation and filtered; it is then boiled with 40 grs. of sulphuric acid and 150 grs. water for half an hour, filtered, evaporated and set aside to crystallize. As it is requisite always to employ a slight excess of sulphuric acid, in order to decompose the iodate of barytes entirely, the crystallized iodic acid generally contains some sulphuric acid; it is redissolved, boiled with a small quantity of iodate of barytes, the filtered solution evaporated to dryness, and cautiously heated for a few hours, (to remove the nitric acid derived from the precipitant) until no more white vapours escape, when it is redissolved and again concentrated. No distinct crystals, however, are now obtained, but only crystalline crusts; for, as was long since observed by Serullas, *pure* iodic acid crystallizes with great difficulty.

Hydrate of Iodic Acid.—It is not yet positively decided whether the solid iodic acid is an hydrate (Berzelius) or anhydrous (Mitscherlich, Rammelsberg). According to the author, there are two distinct hydrates, but iodic acid likewise exists in the anhydrous

state. Iodic acid, crystallized from aqueous solutions, is IO^5, HO ($3IO^5$, 3HO), and is soluble in every proportion in water and in alcohol. On being heated for some length of time at a temperature of 86° to 104° in dry air, or more rapidly at 266°, it parts with two-thirds of its water; which likewise takes place when it is treated with absolute alcohol, or with alcohol and sulphuric acid. It is then $3IO^5$, HO, is still soluble in water, in which it immediately passes into the first hydrate, but insoluble in alcohol. Both hydrates part with the whole of their water at 338°, and are converted into anhydrous acid, which is transformed into the first hydrate by water and alcohol of 0·85 spec. grav.

When a syrupy solution of *pure* iodic acid is allowed to cool between 50° and 95°, a dull white crystalline mass is obtained (in the presence of any foreign acid, beautiful crystals), which is not altered under a bell-glass over sulphuric acid at 59°. This mass lost in the metallic bath, in four experiments, 5·43, 5·87, 5·17, 5·68 per cent. water; the formula IO^5 HO requires 5·13. It must be heated to a temperature of 338° before it parts with the whole of its water; the dehydrated acid is therefore decomposed, when all organic substance is excluded, far above the boiling-point of mercury; but since the entire exclusion of dust is very difficult, a partial decomposition always takes place previous to this temperature, and the experiments to determine the amount of water constantly afford a slight excess. If the acid is not heated to above 266°, or is allowed to stand for some time over sulphuric acid at 104°, it only loses 3·59, 3·88 per cent.; $\frac{2}{3}$ at. = 3·42.

Crystalline iodic acid was conveyed into a tube about 30 centimetres in length; above it was placed a layer of asbestos moistened with sulphuric acid, then some dry asbestos, and lastly a layer of recently-calcined caustic lime; on heating now the iodic acid to decomposition, oxygen gas was alone given off; the water and the iodine remained with the sulphuric acid and the lime. The loss of oxygen in two experiments amounted to 22·57, 22·38; the formula IO^5, HO requires 22·81. On treating the acid, dried at 266°, in the same manner, the loss amounted to 23·42 per cent.; the formula $3IO^5$, HO requires 23·63.

The acid IO^5, HO is readily soluble in alcohol of 0·839 spec. grav., which is likewise the case with the anhydrous acid, while that dried at 266° is nearly insoluble. When some sulphuric acid is cautiously added to the spirituous solution of the hydrate or of the anhydrous acid, and the mixture then boiled, a separation of white glittering spangles takes place, which agree in their composition with the acid dried at 266°. When the solution of anhydrous iodic acid in alcohol is set aside, IO^5, HO separates. Absolute alcohol in no case dissolves the iodic acid, but removes from the first hydrate two-thirds of its water.

Iodates.

Iodate of Potash: a. *Neutral.* Is obtained by saturating iodic acid in the cold with caustic or carbonated alkalies; it loses, on being

heated in a tube filled with asbestos, 22·46, 22·49, 22·47 per cent.; the formula IO^5, KO requires 22·48.

b. *Biniodate*: is obtained by the mixture of the constituents in equivalent proportions and crystallization. It still retains 1 atom water at 266°, but loses it at 302°. The loss in water amounts to 2·3 per cent.; on ignition, 57·37, 57·57 iodide of potassium remained behind. The formula IO^5 KO + IO^5, HO requires 2·31 water and 57·48 iodide of potassium.

c. *Triniodate*: is obtained by treating the preceding salt with an excess of iodic acid. This salt begins to part with water at 338°; it gives off 2·73, 2·71 per cent.; it then undergoes no further change until 464°, when a loss occurs of 0·55, 0·63 per cent.; the formula $3IO^5$, KO + 2HO requires altogether 3·19 per cent. water (the total loss in four experiments amounted to 3·27, 3·28, 3·34, 3·12). At 338° it parts with five-sixths of its water; the salt may therefore be regarded as IO^5, KO + IO^5, HO + IO^5, HO, *i. e.* as a combination of biniodate of potash with hydrate of iodic acid, in which the biniodate parts with its water at 338°, but the third atom of iodic acid is only reduced to IO^5, $\frac{1}{3}$HO. When this salt is heated in the same manner as the free iodic acid, the loss in oxygen amounts to 22·55, 22·47 per cent.; calculation requires 22·68.

d. *Basic Iodate of Potash.*—The author could not obtain the crystalline basic salt described by Gay-Lussac. From a solution of 1 equiv. iodic acid and 2 equiv. potash the neutral salt crystallizes; and even with greater excess of potash the salt, which on ignition loses only 22·34 per cent. oxygen is obtained.

e. *Iodic Acid and Sulphate of Potash.*—This compound, prepared by Serullas, is SO^3, KO + IO^5, HO. Exposed to heat, it loses at first 2·28, 2·5 per cent. water ($\frac{2}{3}$ atom=2·28); the decomposed iodic acid is given off at the same time with the last third of water, and a residue of 22·92, 23·10 per cent. pure sulphate of potash remains; the calculation requires 23·23. The hydrate of iodic acid likewise yields in this combination at first only two-thirds of its water. Analogous to this compound are the combinations of the bisulphate of potash with the hydrate of nitric acid, and with the hydrate of phosphoric acid described by Jacquelin.

f. *Iodate of Potash and Chloride of Potassium.*—This compound, likewise discovered by Serullas, is ClK + IO^5 KO + IO^5 HO. The water cannot be expelled from it without disengaging at the same time chloride of iodine. At 500° it undergoes complete decomposition. When the salt is converted into sulphate of potash, 37·47, 37·57 per cent. is obtained; the calculation gives 37·67.

Iodate of Silver, prepared by precipitating nitrate of silver with iodic acid or with iodate of potash, is white, and remains so if not exposed to a strong light. It tenaciously retains some interstitial water till 392°. On ignition it loses 17·05, 17·03, 17·06 per cent. The formula IO^5 AgO requires 16·99. As the calculation is made with 1579·5, as the equivalent for iodine, the iodate of silver may be regarded as a proof of the correctness of this equivalent.

Iodate of Lime.—When iodic acid is added to a solution of chlo-

ride of calcium or nitrate of lime, minute brilliant crystals separate after a time, which are dissolved in boiling water and recrystallized. The salt contains some water, which is removed by means of blotting-paper; it effloresces slowly in dry air, parts already with some water at 140°, with still more at 212°, but the last portion is not expelled before 374°. The dehydrated salt, decomposed by sulphuric acid, yields 14·35, 14·44 per cent. lime (calculation 14·4). The total loss of the salt, dried between bibulous paper, amounts to 22·4, 22·62 per cent., and the hydrated salt affords 11·15 per cent. lime; the formula CaO, IO^5, 6HO requires 21·74 water and 11·27 lime. Only 18·56, 18·28 per cent. water was expelled at 212° (5 equiv. = 18·11). In another series of experiments the total loss in water was 21·47, 21·49, 21·43 per cent.; the loss at 212° was 17·71, 17·72 per cent. The crystallized salt is therefore IO^5, CaO, 6HO; the salt at 212°, IO^5, CaO, HO; at 374°, CaO, IO^5. We frequently meet with this atom of water, adhering tenaciously, in other salts of lime. The author, supported by the isomorphism between NaO and CaO + HO, and the difference between anhydrous and hydrated sulphate of lime, is induced to regard CaO and CaO + HO as two distinct bases, capable of affording entirely different salts; it is not requisite that an acid should be able to combine with both. Chloride of calcium with 2 equiv. water, belongs to the series CaO + HO, for (CaO, HO) ClH = CaCl, 2HO; the oxychloride of calcium by (CaO, HO) ClH + 3CaO, HO; citrate of lime by $\bar{C}i$, 3(CaO, HO) + HO.

Iodate of Barytes is obtained on adding barytic water to a large excess of iodic acid, and boiling; it is precipitated in the form of a white crystalline powder. Well-washed and dried, it loses at 266° 3·36, 3·43 water, and affords 30·38 barytes; the formula BaO, IO^5, HO requires 3·57 water and 30·36 barytes.

If in the preparation of this salt there be not an excess of iodic acid during boiling, or if it be precipitated from nitrate of barytes or chloride of barium, it retains 1½ to 2 per cent. excess of barytes or of barytes salt, which can in no way be removed by edulcoration. According to Mitscherlich, the same happens with sulphate of barytes when it is precipitated from nitrate of barytes. Iodate of barytes, precipitated from nitrate of barytes or chloride of barium, accordingly affords iodic acid, which retains some nitric acid or chlorine.

Iodate of Strontia is readily precipitated by iodic acid from soluble salts of strontia. It loses at 212° 3·88 per cent. water, and contains 22·49, 22·51 per cent. strontia; the formula IO^5 SrO + HO requires 3·93 water and 22·80 strontia.

Iodate of Soda is the most soluble of all the iodates, and is obtained in the same manner as iodate of potash. It contains a different amount of water according to the temperature at which it was formed. The salt obtained at 158°, and above, is *anhydrous*. All the other hydrated forms of this salt, placed under a bell-glass over sulphuric acid at the ordinary temperature, part with the whole of their water with the exception of 2 equivalents. The salt dried in

this manner generally contains 8·30, 8·39 water and 15·58 soda (calculation, according to $IO^5 NaO + 2HO$, requires 8·31 water and 15·79 soda). If the salt be crystallized at 50°, and the mother-ley be then reduced to 32° Fahr., a salt is obtained, which, placed for a short time on bibulous paper, and then preserved in a bell-glass surrounded by water at 32°, contains 42·15, 42·07 per cent. water (16 atoms=42·15). On keeping this salt at 32°, it gradually loses water until it contains only 35·54 per cent. (12 atoms=35·36). If it be now warmed in a moist atmosphere to between 50° and 60°, the salt after a few days contains only 31·44, 31·51 per cent. (10 atoms = 31·29); this salt sometimes crystallizes from solutions at 43° to 47°. When allowed to crystallize at 68°, beautiful octahedrons separate as long as the liquid is concentrated, which contain 20·55, 21·4 per cent. water (6 atoms = 21·45); subsequently acicular crystals make their appearance with 15·16 per cent. water (4 atoms = 15·4); and lastly, minute silky fasciculi of a salt with 2 atoms water (experiment gave 8·08, calculation 8·31). Probably these various hydrates likewise possess a different degree of solubility in water.

It was found impossible to obtain a basic salt; even when a great excess of soda was present the neutral salt always separated.

Iodate of Magnesia.—Carbonated and calcined magnesia dissolve in iodic acid; the neutral salt separates in crystals on concentrating the solution. It loses no water over sulphuric acid, but when heated parts with 15·95, 16·16 per cent., and contains 10·71 per cent. magnesia (the formula $IO^5 MgO + 4HO$ requires 16·14 water and 11·07 magnesia). Of these 4 atoms of water, $3\frac{5}{6}$ are readily expelled between 212° and 302°; but the last $\frac{1}{6}$th does not escape before 410° to 428° (at this temperature 0·66 per cent. water is expelled). In this therefore it resembles the triniodate of potash, and it appears as if 3 atoms of magnesia combined to a single atom of a new base by exposure to heat, and so formed a triniodate of this new base. The iodate of magnesia, when heated to 482°, becomes extremely difficult of solution; the author is consequently inclined to admit in the magnesia salt with 4 atoms water (and in the chloride with 5 atoms), a base MgO, 4HO, analogous to that admitted for lime, CaO, HO, while in the anhydrous salts the base may be represented by 3MgO. By boiling iodic acid with an excess of magnesia, the author once obtained a salt with 6 atoms water, 2 of which readily escaped by efflorescence.

Iodate of Copper.—This salt exists in various forms, similar in some respects to what Graham observed with oxalate of copper. The author has examined four decidedly distinct kinds of iodate of copper.

First Form.—Iodic acid throws down from soluble salts of copper a voluminous bluish-white precipitate, which redissolves on agitation or on the addition of water; but if it be allowed to stand or be warmed, it becomes more compact, granular, darker and insoluble; the supernatant liquid likewise becomes turbid, and deposits a fresh quantity of the insoluble granular compound. While the

insoluble compound can be washed and dried without alteration, the soluble form, pressed quickly between blotting-paper, can only be preserved for a few minutes without undergoing the above change. The first form, which certainly contains more water than the insoluble modification, cannot be submitted to analysis. If oxide of copper be precipitated by caustic potash at 32° and washed at 32°, it dissolves readily in the cold in iodic acid; but the solution soon becomes turbid, and deposits an insoluble salt. In all cases where precipitates form very slowly, there probably exists a soluble and an insoluble form; the difference between the two may depend on the amount of water, but also on a modification of the base.

Second Form.—The insoluble salt, the formation of which has been above described, always contains a small per centage of the copper salt employed; it is obtained direct and pure by pouring the solution of a copper salt into iodic acid, or by treating carbonate of copper or the hydrate of the oxide of copper, both recently precipitated, with iodic acid at 59° to 68°. The pure salt contains 1 atom water, which it does not part with before 464°; the loss amounts to 4·32, 4·54 per cent.; the anhydrous salt contains 19·3 per cent. oxide of copper; the formula IO^5, CuO, HO requires 19·22 CuO and 4·16 HO. Any retained sulphuric acid may be readily determined by destroying the salt with concentrated muriatic acid, as soon as chlorine is disengaged diluting the liquid and placing some zinc in it, and after complete destruction precipitating the sulphuric acid by nitrate of barytes. The salt is of a bright blue colour, but green when it contains iron. The base in it is probably CuO HO.

Third Form.—Oxide of copper, which has become black by long edulcoration, preservation for fifteen to twenty-four hours, or by boiling with water, is converted by iodic acid into a greenish-gray powder, which is not further changed. This powder is a salt which loses 3·19, 3·37 per cent. water at 518° to 536° ($\frac{2}{3}$ atom = 2·83); the anhydrous salt contains 19·22, 19·32 per cent. oxide of copper. The author regards it as a salt of the base 3CuO, analogous therefore to the triniodate of potash, viz. IO^5, 3CuO + $2IO^5$ HO.

Fourth Form.—Oxide of copper, which has been exposed to a red heat for several hours, appears to undergo no change on being treated with iodic acid; there is however a salt formed of a black colour, which is easily washed. At 518° to 536° it parts with 2·58, 2·61 per cent. water, and contains 29·7 31·22 oxide of copper. The formula IO^5, 6CuO + $2IO^5$, HO, in which a base, 6CuO, is admitted, requires 31·49 CuO and 2·38 HO. If the salt be boiled for some length of time with iodic acid, it passes into the third form.

Iodate of Ammonia.—The neutral salt constantly loses ammonia. The acid salt detonates at 338°, without previously giving off water.

Iodate of Iron is likewise only of transitory existence.

The author regards this investigation as a contribution to a mode of examination of salts which may be placed by the side of Graham's; with this difference, however, that while Graham reduces everything to the various states of the acids, we here find several important illustrations of the influence which various states of the bases may

exercise or have on the constitution of salts. The author intends to follow up these inquiries.—*Ann. de Chim. et de Phys.*, t. ix. p. 400.

Preparation and Analysis of the Hyperoxide of Silver.
By M. WALLQUIST.

The hyperoxide was prepared according to Ritter's method, by the action of a powerful galvanic battery on a solution of nitrate of silver; it is deposited at the positive pole, the more distinctly crystalline the slower the action. The author employed for this purpose a tube bent in the shape of a horse-shoe, into the arms of which the wires were inserted water-tight by means of corks, while the curve directed upwards contained an aperture for the escape of the liberated oxygen gas and for introducing the concentrated solution of silver. The peroxide separates readily from the wire, crystallizes in octahedrons, is blackish gray, brittle, is not decomposed by water at the ordinary temperature, and is soluble in oxyacids with disengagement of oxygen, and in muriatic acid with evolution of chlorine. When mixed with phosphorus and sulphur, it detonates on being struck. By exposure to heat in a glass bulb, it loses 12·77 per cent. oxygen. The formula AgO^2 requires 12·89 per cent.—*Journ. für Prakt. Chem.*, xxxi. p. 179.

On the Cause of the Acidity of Human Urine.

Our readers will recollect that, at page 206 of this volume, we gave an account of Prof. Liebig's experiments, showing the presence of benzoic acid in the urine, &c.; we will now give an abstract of his method of disproving the ordinary opinions on this point.

Direct experiments show that fresh urine, of a strongly acid reaction, and taken from various healthy individuals, when cautiously neutralized with water of barytes, does not retain in solution the least trace of barytes. Now, as lactate of barytes is readily soluble in water, the urine would certainly, and of necessity, contain barytes, if its acid reaction were really owing to the presence of lactic acid. Upon the addition of the first drop of the barytic water to urine, an extremely copious precipitate is formed, which consists of urate and phosphate of barytes and lime; but no detectable trace of barytes is found, even although only just so much barytic water is added as to leave the urine still possessing a feebly acid reaction. Carbonated and calcined magnesia act upon urine in precisely the same manner. If either of these substances be mixed with water, so as to form a milky fluid, and then be added to an acid urine, the acid reaction will immediately cease, and a very copious white precipitate be formed. The fluid now manifests a feebly alkaline reaction, and contains a trace of magnesia in solution. It is a remarkable circumstance that magnesia withdraws the phosphoric acid from the urine so completely, that a mixture of perchloride of iron and acetate of potash no longer indicates a trace of phosphoric acid in the urine which has thus been treated with magnesia. Prof. Liebig also in-

stituted direct experiments to detect lactic acid. These were made upon putrid urine, because lactic acid is not destroyed by putrefaction, and must therefore, of necessity, be present in putrid urine if it really forms a constituent of fresh urine. The experiments of Berzelius on this point do not, any of them, amount to a positive proof that lactic acid really forms a constituent of fresh urine. Liebig's mode of proceeding for the detection of lactic acid was the following:—Putrid urine was evaporated to dryness in a water-bath; the residue treated with a mixture of alcohol and sulphuric acid. The fluid obtained was saturated with oxide of lead, then filtered to separate the phosphate, sulphate and chloride of lead formed; the lead contained in the filtered liquid was separated by sulphuretted hydrogen. The solution, which would have contained lactic acid had there been any present, was evaporated in a water-bath, and the residue treated with alcohol; a quantity of common salt remained. The soda was removed from the alcoholic solution by effloresced oxalic acid at a high temperature; the oxalate of soda separated by filtration; the fluid was then saturated with oxide of lead, which again gave rise to the formation and separation of chloride of lead. The solution was again freed from lead by sulphuretted hydrogen, then concentrated in a water-bath, and basic acetate of lead added in excess; a copious white precipitate was separated by filtration. The fluid must have contained the lactic acid had any been present in the urine; the lead in solution was separated by sulphuretted hydrogen, the fluid filtered, evaporated in a water-bath, and boiled with hydrate of barytes; a quantity of ammonia was evolved by this operation. After the decomposition of the ammoniacal salt, the new-formed salt of barytes was cautiously decomposed by sulphate of zinc, and every possible means was applied to obtain crystals of the lactate of zinc from the fluid, but without success; no trace could be discovered. The white precipitate, obtained by means of the basic acetate of lead, contained hydrochloric acid and a brown resinous substance, which upon combustion comported itself like an animal substance. Other methods of analysis were adopted, but with no more success. The experiments were made upon from 40 to 50 lbs. of urine. All the experiments indicated the presence of an organic acid; but after the removal of all the inorganic acids and bases contained in the urine, this acid was proved to be a mixture of acetic acid with a brown, highly-nitrogenized substance, which is a product of the putrefaction of the urine. Respecting the cause of the acidity of healthy urine, Liebig remarks, that the bibasic phosphates of soda and potash are, in many respects, highly remarkable salts; although of a tolerably strong alkaline reaction, yet they exercise no destructive action upon the skin or upon organic formations. They possess all the properties of the free alkalies, without being such; thus they absorb carbonic acid, and this in such a manner that acids produce effervescence in a saturated solution of this kind, just as in alkaline carbonates. Hippuric acid dissolves with facility in water to which common phosphate of soda has been added; uric acid possesses the same property at a high temperature;

the phosphate of soda, in this process, loses its alkaline reaction completely upon the addition of uric and hippuric acids, and becomes acid. The acid nature of the urine in man and the carnivorous and graminivorous animals is thus explained in a very simple manner.—Liebig's *Lectures*, abridged from the *Lancet*, June 1st and 8th.

CHEMICAL PREPARATIONS.

On the Preparation of Chlorine Water, and on the Determination of its Amount of Chlorine. By M. A. Buchner, Sen.

[Continued from p. 314.]

Testing of Chlorine Water:—

1st. *For Metals.*—This is best effected by evaporation.

2nd. *For Muriatic Acid.*—Pure chlorine water does not effervesce with carbonate of potash. The test with calomel, recommended by Wackenroder and Herzog, has been recently described (vol. i. p. 461).

3rd. *As to its real Amount of Chlorine.*—The chlorometric methods known do not suffice in this instance, since they only afford accurate results when a ready-made sample is at hand for comparison and graduating the tube. Wittstein has made the following experiments, to ascertain whether the metals would serve in this case for determining the amount of chlorine:—

The first experiments were made with copper, since this very readily combines with chlorine, and is the cheapest of the metals that could be used for the purpose. 270 grammes of the ordinary officinal chlorine water were weighed off in a small flask provided with a glass stopper, and a bright, accurately weighed slip of copper placed in it. The flask was closed air-tight, folded in paper, and placed in a dark position, shaking it daily, removing the stopper and smelling. Ten days elapsed before the smell of chlorine had wholly disappeared, and not only had protochloride of copper formed, which partially covered the slips of metal and protracted the process, but there was also some perchloride of copper in the solution, to which it imparted a bluish colour; and lastly, on removing the protochloride, the pieces of metal were seen to be covered with a blackish layer, which was probably a subchloride, and could easily be removed with muriatic acid. It was however attempted to calculate the amount of the chlorine in the water from the loss in weight which the slips of copper had undergone, presupposing that the perchloride and subchloride compensated for each other, and consequently that the whole of the chlorine was present in the state of protochloride of copper. But the result of this calculation was only 2·299 chlorine in 1000 parts by weight, which seemed to be too little.

Notwithstanding this not altogether favourable result, the author nevertheless believes that the copper test is especially adapted for

the quantitative determination of the free chlorine, and that it only requires some improvement in the process to answer completely. For instance, in order to shorten the time, it would only be requisite to increase the surfaces of contact, to take therefore instead of foil either filings or precipitated copper, to assist the perfect formation of the protochloride towards the end by gentle heat, and to add some muriatic acid in order to dissolve the whole of the chloride as protochloride of copper, and thus facilitate the weighing of the metallic residue.

Since mercury is divided, on shaking with an aqueous liquid, into extremely minute globules, and thus presents considerably more points of contact than the compact copper, it might be expected *à priori* to be extremely well-adapted for the determination of the amount of chlorine in chlorine water, so as to arrive at a result in a short time; but in this case the chlorine must be calculated from the increase in weight of the mercury, an insoluble protochloride being formed. For this purpose 4320 grains of ordinary chlorine water, more than four weeks old, were shaken continuously with 185 grs. of mercury. In two hours the smell of chlorine had already disappeared, and the mercury had become converted into a gray powder, which well-dried weighed 187·20 grs., so that from this increase in weight only 0·50 chlorine could be calculated for 1000 chlorine water, which was evidently a perfectly false result. The reason of this however was soon detected, for the liquid filtered from the gray mercury, and from which no metallic globules were deposited, was distinctly acid, and contained mercury in solution, which, on being precipitated with protochloride of tin, amounted to 10·40 grs., and corresponded to 12·20 grs. protochloride of mercury, or 14·00 of the perchloride. In order therefore to determine from the experiment the quantity of chlorine combined with the mercury, the 12·20 grs. protochloride of mercury had to be added to the above 187·20; we have therefore in all 10·88 grms. chlorine in 3360 grms. chlorine water, therefore 3·238 in 1000—a proportion which approximated more closely to the truth than the results of the copper test, but nevertheless was certainly not exact. The considerable quantity of perchloride of mercury which had remained in solution during this experiment, led to the belief that the amount of the metal might be proportionately raised, and ought to be increased until globules of mercury separated, in order to convert the whole of the chlorine into insoluble protochloride. There was moreover a certain excess of metal present in the gray precipitate, which was evident from the colour; but the extremely minute globules in it appear to be so inclosed by a coating of calomel, that they could no longer act on the dissolved chloride.

To settle this point at once, the experiment was repeated with a freshly-prepared chlorine water; for which, however, in order to compare the proportions of saturation, only 9 oz. of muriatic acid of the given strength, and 3 of manganese to 6 lbs. (112 oz.) water had been employed, and not 12 oz. of muriatic acid and 4 of manganese as usual. This water appeared, as far as could be judged from its colour and

odour, to be well-saturated. 9 oz. of it were shaken with ½ an oz. of mercury, which was very soon converted into a gray powder, from which no more metallic globules separated; on that account therefore a larger quantity of mercury was poured into it, and the shaking continued until all odour of chlorine had disappeared. When placed aside for some time, some metallic mercury separated from the gray powder, proving that this time a sufficient quantity had been present to precipitate the whole of the chlorine as calomel; and, in fact, there was no longer a trace of mercury to be discovered in the filtered liquid, for sulphuretted hydrogen as well as protochloride of tin produced no change; nor was there any muriatic acid in the chlorine water, for blue litmus-paper was not reddened, and only a very slight turbidness resulted with nitrate of silver. In order to determine the amount of chlorine, the gray precipitate, together with the metallic mercury, was collected, dried and weighed. There were found 13·1 grs. chlorine, which had combined with the mercury; from which was found by calculation 3·03 chlorine for 1000 parts, or 1·454 gr. in an ounce of the chlorine water sample. As this amount does not indicate a well-saturated water, it results that in order to effect this we must either pass a considerable excess of gas into the water, or apply more than the ordinary pressure.

This experiment proves however that the whole of the free chlorine may be removed from an aqueous liquid by shaking with metallic mercury, if the metal be used in such excess that a portion of it separates in the free state. If, on employing an insufficient quantity of mercury, soluble chloride (corrosive sublimate) should have formed, then it is only requisite to increase the amount of metal to precipitate the whole of the chlorine compound. Of this the author convinced himself by another experiment, which showed that corrosive sublimate, shaken with excess of mercury in an aqueous solution, is entirely precipitated, and that the filtered liquid no longer contains a trace of chlorine or mercury.

Since calomel forms, by shaking with chlorine water, an equivalent of perchloride corresponding to the amount of free chlorine present in solution, it may likewise be employed for determining the quantity of chlorine in chlorine water. The author also intends to make experiments on this point.—Buch. *Repert.*, xxxi. p. 164.

Preparation of the Tartrate of Protoxide of Iron.

M. Bolle has observed, that 4 parts sulphate of iron and 3 parts tartaric acid dissolve in water at the ordinary temperature to a perfectly clear solution, but on being heated prototartrate of iron separates as a bluish-white powder, which again disappears on cooling. To collect this compound, therefore, it is requisite to boil the mixture, allow it to subside, to decant rapidly the liquid, which operation must be frequently repeated, when the precipitates are washed with boiling water. The prototartrate of iron is obtained more easily and in the form of an olive-green powder, by decomposition

of the protochloride of iron with neutral tartrate of potash. Both preparations are anhydrous, and afford 40·6 per cent. peroxide of iron.—*Archiv der Pharm.*, xxxvii. p. 33.

Preparation of pure Nitrogen.

Pure nitrogen gas is obtained in abundance, according to E. Marchand, by submitting to distillation in a retort a solution of chloride of lime and caustic ammonia.—*Journ. de Chim.*, p. 15.

Prestat's Adhesive Plaster.

The following composition is said never to crack, and not to inflame the skin:—*Empl. Diachyl. Gum.*, 400 grs., Purified Rosin, 50 grs., *Tereb. Venet.*, 38 grs. are mixed together at a gentle heat, and then 12 grs. of *Gum Mastich* and 12 grs. of *Gum Ammoniac* incorporated, and the mass spread on linen. In winter it is advisable to add 10 grs. more turpentine and 12 grs. of *Ol. Amygdal.*—*Gaz. des Hôpitaux*, t. vi. No. 35.

Preparation of Carbonate of Potash, free from Silica, from ordinary Pearlash. By Prof. Juch.

1 lb. of crude potash is dissolved in 1 lb. of rain water, and 4 oz. of finely-pulverized vegetable charcoal added to it; it is left for twenty-four hours, being frequently stirred and then filtered. On evaporation and saturation with an acid, it will be found not to contain a trace of silica, which it is otherwise so difficult to remove.—*Journ. für Prakt. Chem.*, xxx. p. 320.

Pills and Boluses of Copaiba.

To form balsam of copaiba into pills and boluses, J. F. R. Simon recommends wax. He employs the following proportions, which have been very generally adopted. For pills:—Liquified white wax, ʒj.; balsam of copaiba, ʒij.; powdered cubebs, ʒiij. For boluses:—Liquified white wax, ʒj.; copaiba balsam, ʒiij.; powdered cubebs, ʒvj.—*Archiv der Pharm.*, xxvii. p. 334.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Source and Nature of Colouring Substances of Organic Origin, and on the Action of Oxygen upon them. By F. Preisser.

Extraction of the Colouring Principles in a State of Purity.

Hitherto but very few of the colouring principles have been obtained well-crystallized and sufficiently pure to be submitted to elementary analysis. White and blue indigotine, alizarine, luteoline, morine and hematoxyline are those which we are acquainted with in

a crystalline state. The others offer merely traces of crystallization, or possess the form of an extract; such are carmine, santaline, curcumine, carthamine, bresiline. And lastly, the greater number are still unknown; the colouring principles of the annotto, of the Persian berry*, of the fustic, &c.

According to M. Chevreul, the coloured portions of vegetables contain simultaneously several distinct colouring principles, which render their extraction in a state of purity very difficult: thus the red principles are always accompanied by yellow, and these are ordinarily associated with fawn or brown substances. These opinions have hitherto been entertained by most chemists; thus we find admitted in fustic two tinctorial principles, yellow morine and white morine; in Carthamus, a yellow principle distinct from the red one, or carthamine; in quercitron, quercitrine or yellow principle, and a reddish-brown principle; in madder, several red principles, a yellow principle, a brownish substance, &c.

The first thing to be ascertained was, whether these different principles, contained in the same tinctorial substance, are not simply modifications of one and the same. The processes generally adopted for the extraction of colouring substances consist in treating the ingredients with alcohol or æther and evaporating the liquids, which sometimes deposits the substances in a crystalline state, but most frequently in the form of powder or extract. The exhaustion of vegetable substances with water affords very complex products, from which it is difficult to remove the foreign bodies. The following is the process which we first employed:—

The tinctorial substance was treated at different intervals with alcohol or æther, according to its degree of solubility in these solvents. Triacetate of lead, added to the liquor, precipitated its colouring matter, and formed an insoluble lake, differing in colour. After the deposition of this salt, the supernatant liquid, which is generally quite colourless, was decanted. The lake was well-washed, and suspended in a sufficient quantity of distilled water, and submitted to a current of sulphuretted hydrogen gas in excess. The liquid was filtered and evaporated under the receiver of the air-pump.

This method furnished us with a great number of colouring principles, free from colour and in very regular crystals. Sometimes, indeed, evaporation *in vacuo* was useless, the crystals being deposited in the vessels in a few seconds, especially when the liquids were filtered hot.

This process had one inconvenience, that of leaving acetic acid in the liquors. The crystals were deposited with difficulty from these acid liquors, and it was almost always impossible to purify them. The following is the method which we now adopt:—

The tinctorial substance is treated with water, alcohol, æther, or a slightly alkaline solution; the coloured liquors are agitated with well-washed hydrate of lead, obtained by decomposing the nitrate of lead by caustic ammonia. The colouring matter is deposited

* The author was evidently unacquainted with Dr. Kane's researches on this subject. See Phil Mag., vol. xxiii. p. 3.—Ed. *Chem. Gaz.*

frequently in the state of insoluble salt of lead in the cold, but it sometimes requires the assistance of a gentle heat, and the liquors are completely decolorized.

The lakes obtained are the less coloured the more recent the tinctorial matters employed. Thus, with yellow and red woods, the interior or the heart of the wood, which is generally but little coloured, especially when in thick fragments, give lakes of a bright, but not of an intense colour. Fresh madder roots also give a lake of a reddish-yellow colour.

In every case, by acting in this manner, and by passing an excess of sulphuretted hydrogen through the lead salt, a colourless liquid is obtained, from which, by spontaneous evaporation in vessels covered with paper, or by evaporation *in vacuo*, the colouring matters are obtained in the state of colourless crystals.

The Lakes are Salts.

All colouring matters, whether free from colour or coloured, have, when they are quite pure, a perceptibly acid reaction. We have been led to consider the lakes as true salts by the following observations:—

When some quercitron is boiled in water, and the dark brown solution agitated with hydrate of lead, the tannine having been first separated from it by a little gelatine, an olive-brown precipitate is obtained with a small quantity of hydrate, and the supernatant liquor is of a beautiful golden yellow. If this be agitated with a fresh amount of hydrate, a new lake, of a magnificent golden colour, is produced, which is deposited on the former by virtue of its less degree of density. Lastly, if a small excess of hydrate is added, it falls to the bottom of the vessel, without becoming coloured and without entering into combination. It appeared evident that the density of the two lakes, the one formed by the highly-coloured substance, the other by the lighter-coloured matter, should be different. Elementary analysis subsequently proved that the more the principle is oxygenized and coloured, the greater is its capacity of saturation. This explains the difference of density observed.

The lakes are true salts in definite proportions, for on agitating any one of the colouring principles with a little hydrate of lead, avoiding an excess, well-washing and drying the precipitate, the same weight of oxide of lead is constantly obtained for the same quantity of salt at the same degree of oxidation, by igniting it in a porcelain crucible. The higher the substance is oxygenized the greater is this quantity, as will subsequently be seen from some analyses.

The different Colours occurring in Organic Tissues are but modifications of one and the same principle.

There cannot be the least doubt of processes of oxidation and of deoxidation, analogous to those which we produce artificially in our laboratories when acting upon organic substances, occurring during the act of vegetation. The roots appear possessed of very decided reducing properties, while opposite powers appear to reside in the

flowers: this is very evident from the experiments described by Persoz*, made on balsams with a solution of sulphate of indigo.

The various tints which flowers present, and which pass one into the other with such ease by contact with the air, are evidently effects produced by the action of the oxygen on the primitively-colourless juice circulating in the vessels. Many flowers when first opened are either white or rose-coloured, and become subsequently blue by exposure to the air; others, without colour while in the bud, gradually acquire a yellow colour as they expand, and when dying acquire a brown tint. In all flowers the coloration is always more intense at the circumference than at the centre, that is, where the action of the air and the light is most decided. It becomes therefore probable, as observed by M. Virey†, that the oxidation of the juices is effected towards the circumference of the petals rather than at the pollinic centre of flowers, and that their yellow colour should be less oxygenized than the red, blue or other tints surrounding it. Certain it is that the roots allow only of colourless or slightly-oxygenized liquids penetrating into plants, and that these liquids becoming more and more coloured in proportion as they are exposed to contact with the air, all the modifications observed in the same plant are derived from one and the same principle at various degrees of oxidation.

When the colouring principles are treated as above described, sulphuretted hydrogen acts upon them in removing a portion of their oxygen. A true deoxidation is effected, for when an excess of this gas is passed into a clear and limpid solution of a pure colouring principle, sulphur is always deposited. On evaporating slowly the colourless liquid in the vacuum of an air-pump, so as to remove all the gas it may still hold in solution, colourless or but very slightly-coloured crystals separate, in which it is impossible to detect the least trace of sulphuretted hydrogen. This decidedly proves that the decoloration by sulphuretted hydrogen is certainly not owing, as some chemists have asserted, to the combination of this gas with the colouring principle.

If these colourless principles are now exposed to the air, they become more and more coloured; but they arrive at a stationary tint, which the prolonged action of the air, and especially of the sun, cause to disappear. This coloration is very rapidly effected, and in an energetic manner, under the double influence of the air and an alkali, especially ammonia. Thus the *yellow morine* is only modified white morine; the brown principles of the Persian berry, of the quercitron, of the fustic, are only more advanced states of oxidation of the yellow principles of these substances. Admitting, moreover, that some foreign principles, amongst others tannine, which always accompany the colouring matters, become more or less coloured by the air, and the diversity of tints of the organs of plants containing the tinctorial matters will not appear surprising.

* Introduction à l'Etude de la Chimie Moléculaire, p. 553.

† Remarques sur les Variétés des Couleurs des Fleurs et leurs Causes.—*Journ. de Pharm.*, xxiv. p. 661 (1838).

Characters of the Colouring Principles.

Red Principles.

Bresiline.—This principle, to which the woods known in commerce and in the drug trade by the names of Brazil wood and Fernambuc owe their red tinctorial properties, was discovered by M. Chevreul, who obtained it in the same manner as hematine, by treating Brazil wood with alcohol. This process, however, furnishes it in a very impure state. It may be obtained by the process above described, from the interior and slightly-coloured portion of the Brazil wood, in a very pure state; it is then colourless, in small acicular crystals, which appear to be rectangular prisms; it has at first a sweetish, and subsequently a slightly bitter taste; it is soluble in water; its solution keeps for a considerable time without undergoing any change; it becomes, however, subsequently yellow, and at the margin of a brilliant red. This colouring is manifested more rapidly on boiling the solution, which then becomes of a beautiful crimson; and on allowing it to evaporate, it deposits a multitude of very beautiful brilliant red needles of a satin lustre. We shall call this red-coloured Bresiline, Bresileine.

Bresiline is soluble in alcohol and in æther; hydrochloric acid, with access of air, colours it of a brilliant red; sulphuric acid dissolves it with a yellow colour, but it soon becomes black; dilute nitric acid reddens it very considerably; when heated, it disengages red vapours, with production of oxalic acid. The action of chromic acid and of the alkaline chromates is highly remarkable, and tends to explain several important applications in the manufacture of printed calicoes. On placing some chromic acid or finely-pulverized bichromate of potash in contact with a concentrated solution of bresiline, a lively effervescence ensues, and a considerable quantity of formic acid may be collected by distillation. At the same time the liquid assumes a brownish-red colour, which gradually becomes deeper, and after a few hours a dark crimson-red lake separates. This lake consists of the modified colouring substance bresileine and of oxide of chrome. It is not very stable; for a few washings with water, slightly acidulated with hydrochloric acid, remove the whole of the colouring principle, leaving behind pure oxide of chrome.

For some years very full and varied tints have been obtained by printing over the colours derived from colouring woods with bichromate of potash in a pasty state. Wherever the salt has come in contact with the red principle, the colours, especially after fixation by steam, become deeper and acquire great brilliancy. The chromate is reduced, and it is easily proved that a combination of the modified colouring principle and of oxide of chrome has remained fixed on the stuff; for on treating it with chlorine, a greenish colour is perceptible wherever the chromate has been applied.

This decomposition of the bichromate of potash on the tissues does not take place at once; it is not entirely effected except under the influence of the steaming. When this decomposition happens

instantaneously, the oxygen of the chromic acid decolorizes the tissue; this occurs when an acid is imprinted on a blue tissue, passed through chromate of potash.

The effect of the chromate in deepening the tints is very decided on colours obtained from catechu; but in general it is requisite, in the application of this salt, to pay particular attention to the fact, that the colouring principle, which has become modified by it, has much less affinity for the tissue than previous to this alteration; thus very different effects are obtained according to whether the colour or the bichromate is applied first. In the first case, when the salt reaches the colouring principle already combined with the tissue, it darkens the tint in a remarkable manner; in the second, the tinctorial matter, which is applied on the chromate, becomes oxidized, and being then much less soluble in water, does not combine with the tissue, and is carried off by mere washing. In this case the chromate may serve as a *reserve*, in the same manner as the sulphate of copper in the indigo-baths. As to the tartrate and citrate of chrome, which are also used in print-works as *reserves*, their peculiar action should not be attributed to the oxide of chrome, but to the tendency which these salts have to form double salts with the mordants used. These double salts, which are very soluble in water, prevent the fixation of the mordant, and consequently of the colouring matter. In fact, the acid nitrate and citrate of potash or of soda produce the same effect.

The moist crystals of bresiline gradually acquire a dark red purple tint by placing them under a large bell-glass, near a capsule filled with caustic ammonia. By pouring the ammonia directly over the crystals, the coloration is immediately produced. On conveying some crystals of bresiline and ammonia under a bell-glass full of mercury, the coloration is hardly perceptible if the air be excluded.

Potash and soda give with bresiline, in contact with the air, a vinous blood-red colour, which hydrochloric acid precipitates in an hour's time.

Lime-water reddens the solution of bresiline; when this solution is filtered on a paper not washed with an acid, some hours after the paper is of a bright scarlet-red. The nitrate of silver and the chloride of gold are reduced when boiled with bresiline. Acetate of lead gives a yellowish-white precipitate, which becomes brown by desiccation. When a solution of bresiline is heated with sulphuric acid and peroxide of manganese, in an apparatus arranged so that the liquid and gaseous products may be collected, a violent agitation is manifest in the liquor; no gas is disengaged, but the distilled product contains formic acid. The liquid in the retort is strongly red; left to spontaneous evaporation, protosulphate of manganese is deposited, and the coloured mother-waters contain the same modified colouring matter as that obtained with chromic acid.

Bresiline, heated in a small glass tube, is carbonified without giving off traces of ammonia, even when it is mixed with caustic potash.

Practical Observations on the Employment of Baths or Colours of Brazil Wood.

It is necessary to remark, when making colours for application with Brazil wood, that it is essential not to let them grow stale; otherwise they adhere very imperfectly to the stuffs, and furnish bad impressions. These topical colours must be used as soon as they are prepared, in order to obtain full tints, and that the bresiline may oxidize on the tissue during desiccation. This should likewise be attended to with the other colouring substances.

This is not the case with the decoction of Brazil woods unmixed with a mordant, which affords richer colours when it is old. Experience has shown that a stale decoction gives as much colour as double the quantity of a recent decoction. In the dye-houses, the decoctions of Brazil are abandoned to themselves in casks. Everything tends to the belief that these decoctions undergo a fermentation, which in part deoxygenizes them by long exposure to the atmosphere, and causes the deposition of the tannine and other foreign matters which they contain, and which generally injure the brilliancy and solidity of the tints.

Elementary Analysis of Bresiline.

A colourless solution of bresiline was precipitated with hydrate of lead; the white precipitate was dried in a small closed tube filled with nitrogen. 1·61 grm. bresilate of lead left on calcination 0·405 grm. oxide of lead; consequently the atomic weight of the salt = 5542·11.

On analysis with oxide of copper, it was found to consist of—

		Equiv.	
Carbon	49·33	36 =	2734·26
Hydrogen	3·11	14 =	172·18
Oxygen	21·89	12 =	1213·17
Oxide of lead	25·67	1 =	1422·50
			5542·11

Bresileine was likewise precipitated with hydrate of lead, the reddish-brown precipitate exposed for some time to the air, and then dried. Analysed in the same manner, it afforded—

		Equiv.	
Carbon	38·57	18 =	1377·670
Hydrogen	2·42	7 =	86·610
Oxygen	20·15	7 =	719·960
Oxide of lead	38·86	1 =	1388·490
			3572·730

But since, by calcination of the bresileate of lead, nearly twice the quantity of oxide is obtained than furnished by the bresilate, it must necessarily be admitted that the capacity of saturation of bresileine is twice that of bresiline, consequently that the bresileate contains 2 atoms of base. The formula of this salt will therefore be $C^{36}H^{14}O^{14} + 2PbO$, the atomic weight being $3572{\cdot}73 \times 2 = 7145{\cdot}46$.

From the above analytical results, it is evident that when bresiline becomes coloured by contact with the atmosphere, it absorbs 2 atoms of oxygen, and is converted from $C^{36}\ H^{14}\ O^{12}$ into $C^{36}\ H^{14}\ O^{14}$, which then possesses twice the saturating power of the former.

[To be continued.]

Further Observations on the Energiatype. *By* Robert Hunt.

Experience has suggested to me the advantage of adding to the solution of succinic acid and gum, as previously given*, 5 grains of common salt. This preserves the lights very clear, and indeed improves the sensibility of the paper.

When the solution of the sulphate of iron is laid over the paper, it is requisite to keep disturbing it, by rapidly but lightly brushing it up; otherwise numerous little black specks form, which destroy the photograph. If, as sometimes happens, the surface of the picture blackens all over, it must not be concluded that the drawing is destroyed. The whole of this superficial blackness may be removed by immediately washing with a wet sponge. If the lights become in any way discoloured, a little exceedingly diluted hydrochloric (muriatic) acid will restore them to their proper degree of whiteness; but care must be taken that the acid is speedily washed off, or the shadows will suffer.

When, from the shortness of the exposure, the image developes itself slowly or imperfectly, a slight degree of warmth brings out the picture with rapidity and force. Holding the paper a short distance from the fire is the best mode of operating.—*Athenæum.*

PATENT.

Patent granted to Richard Janion Nevill, Llangennech, Carmarthen, *for an improved Mode of separating certain Metals.*

The invention consists in certain processes for separating silver and lead, or either of them, from copper or other metals, or substances with which copper is combined. The author takes refined copper, containing silver or copper, though not pure or refined, in which silver is in combination, and melts the same in the usual manner; and when in a state of fusion pours it into a vessel of cast iron, or other material fit for the purpose, containing melted lead heated to a red heat, or nearly so; the argentine copper is mixed with lead in those proportions, dependent on the quantity of silver in combination with the copper, which are found to be most favourable for the combination of the silver with the lead, by reason of its superior affinity, and which are well known to metallurgists. After such mixing has been accomplished, it is found that the copper (with some portions of silver and lead in combination), as it cools, rises to the surface; it is taken off, when sufficiently cool, by

* See p. 290.

tongs or other mechanical contrivances, or by means of an iron plate, made to fit, or nearly so, the vessel which is used, which plate should be perforated with holes, and should be placed at or near the bottom of the vessel before the copper is poured into it, and kept there till the mixture is effected and the copper partially cooled, when it should be drawn up through the lead by means of one or more handles fixed to it, and which rise above the melted mixture, by which means the greater part of the silver and lead, passing in a fluid state through the perforations in the plate, remain in the vessel, whilst the copper, with such portions of silver and lead as may still be remaining in combination with it, is taken out of the vessel, and should then be broken into pieces of a size convenient for the process of eliquation, such process being the exposure of the compound metal to a heat sufficient to fuse the silver and lead but not the copper, so that the silver and lead in combination run off, leaving the copper comparatively free from either metal. By the process above described, the greatest portion of the silver is retained by the melted lead in the pot or vessel, and thus separated from the copper without the further process of eliquation. Whatever portions of silver and lead are retained in the copper so taken out of the pot or vessel, are separated by eliquation in the following manner:—

The compound metal of silver, lead and copper, whether obtained by the process before described, or by the method at present in use, is placed in tubes or retorts, which may be made of various forms and of different materials; cast iron is preferred, of the length of from two feet six inches to three feet and about six inches square, with a door or covering at one end, made to open and shut, with a small aperture in it for the purpose of allowing the silver and lead to run out. These tubes or retorts should be fixed in a furnace or oven, with a slope or inclination towards the end, to which the door or covering is affixed. A sufficient quantity of charcoal, or other carbonaceous matter, is put in together with the compound metal; and after closing the door or covering, to prevent the admission of atmospheric air, sufficient heat is applied (which should by degrees be increased) to cause the silver and lead to flow out of the compound metal, and to run into pans or other receptacles placed in front of each tube or retort, by which means the oxidation and volatilization of the lead are in a great degree prevented; and from the lead contained by both or either of the processes above described, is separated the silver by the ordinary process of cupellation.—Sealed Oct. 18, 1843.

THE CHEMICAL GAZETTE.

No. XLIII.—August 1, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Examination of some Fumarates, and on the Constitution of Fumaric Acid (Paramaleic Acid). *By* T. Rieckher.

Two isomeric acids are formed by the distillation of malic acid, which are likewise isomeric with aconitic acid obtained by fusing citric acid, and of which one has been proved to be identical with the acid which occurs in *Fumaria officinalis*. The analyses of Pelouze, Liebig and Crasso, have proved that all these three acids in the hydrated state might be represented by $C^4 H O^3$, HO. It was, however, probable that fumaric acid was monobasic, maleic acid, bibasic and aconitic acid tribasic; this has been clearly shown with respect to aconitic acid by Crasso, while the present communication, and one by M. Buchner, to be communicated in our next, prove the correctness of this view likewise with regard to the other two acids. Fumaric acid gives no acid salts with lime, barytes and oxide of silver, which is the case with maleic acid. It will perhaps be best to point out the differences which exist between these acids and likewise those which distinguish them from others.

Fumaric acid forms broad, thin rhombic or hexahedral prisms, maleic acid oblique rhombic prisms; fumaric acid dissolves in 200 parts cold water, maleic acid in every proportion; fumaric acid has a pure acid taste, maleic acid a disagreeable after-taste. Fumaric acid melts with difficulty, and volatilizes not lower than at 392°, passing into maleic acid; maleic acid melts at 266°, boils at 320°, and is converted into fumaric acid; when distilled quickly, it affords a body which melts at 135°, boils at 349°, and has the composition of anhydrous maleic acid. Lime-water is not rendered turbid by either acid; barytic water affords a white precipitate with maleic acid, which however is converted in a few minutes into shining laminæ, which dissolve in an excess of barytic water or of acid. Fumaric acid is not at all precipitated by barytic water; the crystalline deposit, which gradually subsides from concentrated solutions, is extremely difficult of solution in the acid as well as in the precipitant; both behave alike towards chloride of calcium; no precipitate is produced; the lime salt, which slowly separates from concentrated solutions, is of difficult solution. Acetate of lead, added to a dilute solution of maleic acid, produces a white precipitate,

which changes in a few minutes into micaceous laminæ analogous to malate of lead. With concentrated solutions and excess of lead salt, the precipitate solidifies to a pasty mass. Fumarate of lead, prepared from cold and moderately concentrated solutions, forms a white voluminous precipitate, which gradually cakes together, but does not alter its nature; from dilute and boiling hot solutions a great portion of the salt separates in shining laminæ, not dissimilar to malate of lead. Maleic acid, to which ammonia has been added, affords with nitrate of silver a white precipitate, which changes after a time into colourless transparent crystals; fumaric acid affords, under the same circumstances, a white precipitate, which does not undergo any alteration in four-and-twenty hours.

Fumaric acid likewise dissolves in alcohol and æther, and in nitric acid of 1·40 spec. grav.; it is not decomposed by the latter on boiling. Concentrated sulphuric acid does not decompose it in the cold, but at an elevated temperature there is an evolution of sulphurous acid. An alkaline fumarate can be boiled with chloride of platinum without any separation of platinum-black; fumaric acid is not decomposed by a boiling solution of bichromate of potash; hyperoxide of lead, mixed with water and heated, has likewise no action upon it; but when mixed dry with the acid and exposed to heat, there is at first a deposition of moisture on the glass tube, and subsequently a decomposition takes place with incandescence; no odour of formic acid is perceptible.

By its behaviour towards chloride of platinum, it is distinguished from tartaric and racemic acids. The alkaline succinates behave towards persalts of iron like the fumarates; but then fumarate of the protoxide of manganese is scarcely soluble, while the succinate crystallizes; succinate of zinc is very insoluble, while the fumarate crystallizes. Fumaric acid is much more difficult of solution in water, and sublimes without previously melting. A boiling solution of bichromate of potash does not act on fumaric nor on succinic acid, while it decomposes tartaric and racemic acids immediately; citric, acetic and formic acids after some time. It differs by its behaviour towards lime-water from tartaric and racemic acids, but resembles tartaric acid in its behaviour towards a solution of gypsum. Alkaline citrate immediately precipitates a solution of chloride of barium and chloride of calcium, while the fumarates produce no precipitates under the same circumstances. It differs from formic acid by its behaviour towards salts of silver and protosalts of mercury and chloride of platinum; from acetic acid by its salt of copper and of protoxide of manganese, which are insoluble.

The author has analysed a large number of the salts; the following list exhibits the constitution of several of the most important:—

Crystallized fumarate of lead.....	$PbO\,\overline{Fu} + 2aq.$
Tribasic	$3PbO\,\overline{Fu}.$
Sesquibasic.....	$3PbO\,2\overline{Fu}.$
Fumarate of lead with 3 atoms of water	$PbO\,\overline{Fu} + 3aq.$
Crystallized fumarate of barytes	$BaO\,\overline{Fu}.$

Crystallized fumarate of strontia	$SrO\,\overline{Fu} + 3aq.$
Anhydrous fumarate of strontia	$SrO\,\overline{Fu}.$
Crystallized fumarate of lime	$CaO\,\overline{Fu} + 3aq.$
Anhydrous fumarate of lime.....	$CaO\,\overline{Fu}.$
Neutral fumarate of potash	$KO\,\overline{Fu} + 2aq.$
Acid fumarate of potash	$KO\,\overline{Fu} + \overline{Fu}\,HO.$
Crystallized fumarate of soda	$NaO\,\overline{Fu} + 3aq.$
Ditto, precipitated by alcohol	$NaO\,\overline{Fu} + aq.$
Anhydrous at 392°	$NaO\,\overline{Fu}.$
Fumarate of silver.....	$AgO\,\overline{Fu}.$
Fumarate of the peroxide of iron.....	$Fe^2\,O^3\,\overline{Fu}.$

Ann. der Chem. und Pharm., xlix. p. 31.

Action of Sulphuretted Hydrogen Gas on Perchloride of Sulphur. *By* M. Chevet.

When a slow current of olefiant gas is passed through perchloride of sulphur, SCl*, exposed to the sunlight, vapours of the protochloride of elayle are first given off. If the chloride is then gradually heated, its yellow colour changes into a red, it becomes thick, and smells strongly and permanently of a mixture of blackberries and raspberries. It has at first a sweetish, and subsequently acrid taste; after twenty-four hours it deposits brown acicular crystals, which are insoluble in water, alcohol and æther; the alcohol however removes a little of a red oily liquid, which remains behind on evaporation of the spirit. The crystals are then of a chocolate-brown, but they become colourless on paper, which absorbs a very volatile oil; the crystals readily ignite, and burn with a luminous flame, diffusing the odour of sulphurous acid. Sulphuric acid does not alter them, but caustic potash is coloured yellow by them, and leaves a yellow, solid, but viscid residue, which, like the solution, has the odour of cucumbers.

The red liquid, from which the crystals have deposited, separates, on being mixed with water, into two portions, one of which floats on the surface, while the other subsides to the bottom. Alcohol dissolves a portion of it; water precipitates from the solution a dark red powder; on evaporation a red liquid remains apparently unaltered. If the red liquid is heated in a retort, a yellow, volatile oily product is obtained, which possesses a very persistent, acrid and intense odour.

Chloride of sulphur gives, with petroleum and purified oil of turpentine, a tenacious black mass and a reddish-brown liquid, which are perfectly distinct from the substances employed; the reaction is very violent, muriatic acid being disengaged.—Berzelius's *Jahresbericht*, xxiii. p. 39.

* Or rather $S^2\,Cl + S\,Cl$.

Researches on Butyrone. By M. G. CHANCEL.

M. Chevreul was the first chemist who submitted butyrate of lime to dry distillation; among other products he pointed out the formation of an aromatic volatile oil, presenting an odour analogous to the essential oil of the *Labiatæ*; but owing to the small quantity obtained, this oil has never been submitted to examination.

M. Lœwig has however expressed an opinion relative to the nature of this product. According to him, the formula for anhydrous butyric acid is $C^7 H^6 O^3$; by the distillation of the butyrates, butyrone $= C^6 H^6 O$ would be formed. This formula for butyric acid is now however quite inadmissible, and it will also be seen that no substance, the composition of which can be represented by the formula $C^6 H^6 O$, is ever obtained by the distillation of a salt of butyric acid.

Butyrate of lime, submitted to the action of heat, offers one of the most simple examples of decompositions of this kind. If a small quantity of the pure and anhydrous salt is heated with precaution, it soon decomposes into carbonic acid, which remains combined with the lime, and a volatile oil, which distils over. This oil is nearly pure or scarcely coloured butyrone; the residue is perfectly white and pure carbonate of lime. Not the least trace of a carbonaceous residue is formed on operating upon a few grammes of substance, taking care not to exceed the temperature requisite for the formation of butyrone. Most frequently there is no disengagement of gas, except the temperature be raised too high, in which case the quantity of the gaseous products usually amounts to 3 or 4 per cent. of the weight of the butyrate; the greater portion consists of bicarburetted hydrogen absorbable by sulphuric acid. In no case is there the least disengagement of water if the operation is made on anhydrous butyrate, a fact worthy of attention. However, on distilling somewhat considerable quantities of substance, the operation is far from being so simple; it is impossible to avoid the deposition of a certain proportion of carbon, and the liquid products are always strongly coloured; which should probably be ascribed to the subsequent decomposition of the formed butyrone, owing to the unequal diffusion of heat in the mass. In this case a mixture of several liquid substances is obtained, in which however butyrone is the dominant product. 100 parts of anhydrous butyrate of lime afforded from 42 to 43 parts of crude butyrone.

When this crude liquid is submitted to distillation, its boiling point is at first below 212°, but ascends rapidly to 284°; the liquid, which passes between 284° and 293°, is collected apart, and is nothing further than butyrone. The portions collected before and after are a mixture of butyrone and of two peculiar substances, the one distilling below 212°, the other above 320°, both of which I propose to investigate as soon as I shall have obtained them in sufficient quantity.

Butyrone, collected between 284° and 293°, presents a constant boiling point; it is again distilled, when it may be considered pure.

It forms a colourless limpid liquid, of a peculiar and penetrating odour, and possesses a burning taste. Its density is 0·23; it boils at about 291°. When cooled by a mixture of solid carbonic acid and æther, it solidifies to a crystalline mass. It swims on the surface of water, in which it is almost insoluble, to which however it communicates its odour; it dissolves in every proportion in alcohol; it readily ignites, and burns with a luminous flame. The action of chromic acid on butyrone is most energetic; it immediately inflames in contact with this acid. It does not become coloured by exposure to the air, although in the course of time it absorbs a considerable quantity of oxygen.

Several analyses of this substance, made with products derived from different preparations, constantly afforded the same results, leading to the formula $C^7 H^7 O$. The density of the vapour confirms this formula; the experiment gave 4·0, which approaches closely to the theoretical number 3·98. The formula $C^7 H^7 O$ represents therefore 2 volumes of the vapour of butyrone.

This composition sufficiently explains the formation of this substance; butyrate of lime, submitted to distillation, is decomposed into carbonic acid, which remains with the base, and into butyrone, as indicated by the following equation:—

$$CaO, C^8 H^7 O^3 = CaO, CO^2 + C^7 H^7 O.$$

Thus the dry distillation of butyrate of lime is not less precise than that of the acetate of the same base; the decomposition is effected with ease, and the quantity of butyrone obtained under suitable circumstances approaches closely to that required by theory. —*Comptes Rendus*, June 3, 1844.

Action of Arsenic on Sheep. By M. Berutti.

[It has been stated by M. Gasparin*, that arsenic in large doses had been successfully administered to sheep labouring under pleurisy, and further, that the substance did not act as a poison on healthy cattle or sheep. The following are the experiments and conclusions of M. Berutti on this subject:—]

On the 24th of January 1843 he took two healthy sheep, aged about four months. To the first he gave 8 grms. (rather more than 2 drms.) of arsenious acid mixed with an equal quantity of salt, and to the second 32 grms. of arsenic (1 oz. 14 grs.) without any salt. Two hours after, the latter animal appeared dull and indisposed to motion, lying down again whenever it was made to walk. Excrement of a pultaceous nature and dark colour was passed. In three hours the belly became tympanitic, the animal appeared very feeble and indifferent to external impressions, and was unable to keep on its legs. It died within the four hours. From the moment of taking the poison it passed no urine, nor ate anything, nor gave any indications of suffering. The first animal also passed no urine, nor did it eat, or have any alvine evacuation from the first. It preserved its

* See this Journal, vol. i. p. 199.

natural liveliness for two or three hours, after which it became feeble and dull, and lay down. At the end of four hours it had tetanic convulsions, and died very rapidly. Thus both animals survived the poison about four hours, there being only a few minutes between their deaths. After death not the smallest material lesion could be discovered in their bodies, except that the lungs and right side of the heart were loaded with dark-coloured and fluid blood. In both, the urinary bladder was empty and contracted. A chemical analysis of the organs showed the presence of arsenic throughout the body. The entire absence of the urinary secretion fully confirms the observation of MM. Danger and Flandin, who have maintained that this secretion is suspended in acute poisoning only, and not in the chronic. The author next discusses the action of arsenic, which he pronounces to be depressing on the heart and arteries, and should be treated with stimulants, as alcohol, opium, &c., in various forms of combination. He also endeavours to show that arsenic has no action on the brain, the intelligence having remained entire up to the moment of death, and no morbid lesion being discoverable in that organ. In conclusion, he says, "If the discovery which M. Orfila believes he has made of the normal presence of arsenic in the bones and other tissues of the body had been verified, we should have had to inquire what amount of this substance may be present without being poisonous, and how a substance naturally entering into the formation of the tissues could act as a poison when presented to the absorbing vessels in a much larger proportion than what the system, in its natural condition, would refuse to take up; but as this supposed discovery has been proved to be groundless by the experiments of MM. Danger and Flandin, I will not enter upon the subject."—From an Italian Journal; *Edinb. Monthly Journ.* for May 1844.

On the Decomposition of Hydriodic Æther by Heat. By M. E. Kopp.

M. Gay-Lussac remarked, while investigating the properties of hydriodic æther, that this liquid, on being passed through a tube at a dull red heat, gave rise to the formation of a solid substance, heavier than water and undecomposable by the caustic alkalies. The nature of this compound has hitherto remained undetermined.

The best process for the preparation of the æther ($C^4 H^5 I$) consists in dissolving iodine in alcohol of 0·848 spec. grav., adding phosphorus to it until the colour has disappeared, introducing more iodine and then phosphorus, taking care to cool the liquid, so as to avoid too great an elevation of temperature. This is continued until phosphuretted hydrogen is liberated (the not inflammable $P^2 H^3$). On distilling, nearly the whole amount of æther indicated by theory is obtained; the residue consists of a very acid liquid, containing phosphoric, phosphovinic and a little hydriodic acid, and of a solid pulverulent residue of a dark red colour, which is nothing more than the red modification of phosphorus.

Hydriodic æther is decomposed, for the greater part, on being passed through a long narrow glass tube, at a dull red heat, giving off inflammable gases which burn with a brilliant flame, while a solid crystalline substance, coloured reddish-brown by iodine, condenses in the cold recipient. The gases analysed with chlorine proved to be carburetted hydrogen, CH, and hydrogen in the proportion of 2 volumes of the former to one volume of the latter.

To purify the solid substance, it is treated with a boiling solution of caustic potash, which removes the excess of iodine, and the new product subsides to the bottom of the liquid as a yellowish heavy oil, which solidifies on cooling. The liquid is decanted, the dried mass dissolved in boiling alcohol, from which it separates on cooling in long, flexible, slightly yellow and very brilliant acicular crystals. It is purified by pressure between folds of bibulous paper, and exposure for some time to the air. The density = 2·07, but it is difficult to obtain it accurately, from the fused fragments always inclosing cavities. It melts at 158° Fahr. into a yellow liquid, which on cooling solidifies to a crystalline mass; at 184° it begins to be decomposed, and acquires a gradually darker reddish tint, owing to the iodine set at liberty; heated still higher, it boils, and is volatilized, with partial decomposition, giving off abundant vapours of iodine and inflammable gases; the sublimed product, which has a brown colour, affords the primitive crystals on being treated with potash and alcohol.

The substance is very soluble in hot alcohol and æther, but very sparingly in cold, which admits of its being obtained in beautiful crystals. It is insoluble in water, and neither dilute acids nor alkalies alter it. Concentrated nitric acid immediately disengages nitrous acid vapours, and sets iodine at liberty. Concentrated sulphuric acid only attacks it when the temperature is raised. To determine the iodine, the fused substance was introduced into a long narrow tube, and its vapour made to pass over iron filings heated to redness. Protiodide of iron is formed, which is decomposed with a hot solution of caustic soda, free from chlorides, by introducing the iron filings and the fragments of the tube into the alkaline liquid. After having filtered and washed the precipitated protoxide of iron, the solution neutralized with nitric acid was precipitated with nitrate of silver. The following are the results:—

	I.	II.	III.
Iodine	89·70	89·64	
Carbon			8·40
Hydrogen			1·57

It is therefore iodide of elayle ($C^2 H^2 I$), or the hydriodate of the iodide of aldehydene ($C^4 H^3 I + H I$), which has been so well investigated by M. Regnault; its composition and properties prove their identity.

Some experiments, made with the view of obtaining the cyanide of elayle ($C^2 H^2 Cy$), gave negative results.

On heating a mixture of iodide of elayle and cyanide of mer-

cury, iodide of mercury (Hg I) is obtained, iodide of cyanogen and inflammable gases.

On dissolving the two salts in alcohol, a double salt separates in beautiful white, fusible, acicular crystals, which bear a higher temperature than 176° without decomposing. The products of its decomposition indicate that it is formed of $C^4 H^4 I^2 + HgCy$; for at a high temperature it decomposes into iodide of mercury, iodide of cyanogen, carburetted hydrogen gas, and a slight deposit of carbon.

On heating $C^4 H^4 I^2$ with a very concentrated aqueous solution of potash, the greater part distils over without alteration; but a portion is decomposed into iodine, which reacts on the potash and into CH, which is disengaged.

By using an alcoholic solution of potash, a portion of $C^4 H^4 I^2$ is decomposed, as before, into iodine and into inflammable gas, CH; but the greater part is changed into iodide of aldehydene, or of acetyle ($C^4 H^3 I$), and into H I, which combines with KO.

Iodide of aldehydene is easily obtained by precipitating with water the alcoholic liquid condensed in a well-cooled recipient; $C^4 H^3 I$ is a colourless liquid, of a very strong alliaceous odour, insoluble in water, very soluble in alcohol and æther. It boils at 133°; its density = 1·98. Sulphuric, hydrochloric and nitric acids do not attack it when cold. Fuming nitric acid decomposes it, disengaging iodine and red vapours. On analysis it furnished—

	Found.	Equiv.		Calculated.
Carbon	15·20	4	300·00	= 15·66
Hydrogen	2·00	3	37·50	= 1·95
Iodine		1	1578·29	= 82·39
			1915·79	

The differences observed in the decomposition of hydrochloric and hydrobromic æthers compared to that of the hydriodic æther are readily accounted for. Owing to the powerful affinity of chlorine and bromine for hydrogen, the two æthers, as was well observed by M. Thénard, are decomposed into hydrochloric acid, hydrobromic acid and carburetted hydrogen gas, which are disengaged together, without being able to act one on the other; but iodine having far less affinity for hydrogen, the compound $C^4 H^5 I$ is decomposed into free iodine, and a mixture of 4 volumes of carburetted hydrogen (CH) to 1 volume of hydrogen. Under these circumstances the iodine enters into combination with half the carburetted hydrogen, forming iodide of elayle ($C^2 H^2 + I$), while the rest of the gas is disengaged.—*Comptes Rendus*, May 6, 1844.

Decomposition of Benzoic Acid and of Hydruret of Benzoyle by Contact.

According to MM. Barreswil and Boudault, when benzoic acid is mixed with from 5 to 6 times its weight of pulverized pumice-stone, and is distilled at a temperature not much higher than the

boiling point of benzoic acid, from a retort which is connected with a tube filled with pumice-stone powder, and heated to redness, only benzine and carbonic acid are obtained. If the vapours of the hydruret of benzoyle be passed in the same manner slowly through heated pumice-stone, benzine and carbonic oxide are the products. Benzoate of ammonia affords, under the same circumstances, benzine and carbonate of ammonia. Benzamide gives at a gentle heat hydrogen, nitrogen and hydruret of benzoyle; at a higher temperature, benzine, carbonic oxide, hydrogen and nitrogen. Berzelius had already observed, that benzoic acid was partially decomposed when distilled with sand.—*Journ. de Pharm.* for April 1844, p. 265.

ANALYTICAL CHEMISTRY.

On the Behaviour of the different kinds of Sugars towards certain Reagents. By M. Baumann.

The sugars examined by the author were cane-sugar, diabetic sugar, milk-sugar and mucic-sugar extracted from honey by alcohol. Nitric acid, protoxide of mercury and chloride of platinum had no action on any of them; ammonia, however, threw down a bright red precipitate from the solutions to which chloride of platinum had been added; nitrate of silver was considerably reduced by the last three kinds, but only very slightly by cane-sugar; sulphate of copper, acetate and chloride of copper had their blue colour changed into green by mucic-sugar; ammonio-sulphate, ammonio-acetate and ammonio-chloride of copper were converted into a bright brown colour by the same sugar; all these copper compounds are not affected by the other sugars.

The following combinations of copper afforded characteristic reactions at 212°:—

Sulphate of copper and excess of caustic potash:—with cane-sugar, no reaction; with diabetic sugar, a dirty yellow slightly-orange precipitate (some of the oxide was reduced to the state of protoxide); with milk-sugar, an orange-yellow coloured precipitate, which in forty-eight hours was converted into a tile-red one (the liquid remained clear); with mucic-sugar, a dirty yellowish-red precipitate.

Acetate of copper and excess of caustic potash:—with cane-sugar, a slight red precipitate of protoxide of copper, the liquid clear and colourless; with diabetic sugar, at first a bright orange-coloured precipitate, which after eighteen hours becomes yellow; with milk-sugar, an orange-coloured precipitate, which soon becomes darker, and at last brown; with mucic-sugar, an orange-coloured precipitate, which soon becomes reddish-brown, from reduced protoxide of copper.

Perchloride of copper and excess of potash:—with cane-sugar, a yellow precipitate, of the colour of sulphuret of arsenic, unchanged after eighteen hours; with diabetic sugar, a dark yellow precipitate,

slightly orange, after eighteen hours dirty yellow; with milk-sugar, an orange-coloured precipitate, becoming quickly brown; with mucic-sugar, a dirty orange-yellow precipitate, soon becoming reddish brown, from reduced protoxide of copper.

Protocyanide of copper and cyanide of potassium with excess of potash (prepared by precipitating sulphate of copper with prussiate of potash, addition of an excess of caustic potash and filtration from the precipitated hydrate of the peroxide of iron):—with cane-sugar, the clear colourless liquid acquired after some time a slight yellowish tint; with diabetic sugar, a light brown clear liquid; with milk-sugar, a clear brown liquid; with mucic-sugar, a reddish-brown clear liquid.

Arsenic acid produces with all the sugars a red colour, which is darkest with cane-sugar, resembles raspberry juice with mucic-sugar, becoming gradually brown, and at last black. The cane-sugar, coloured brown by arsenic acid, no longer ferments. The brown solutions afford with sulphuretted hydrogen, yellow sulphuret of arsenic; with nitrate of silver, reddish-brown precipitates, which subsequently become black. Lime-water produces a brown precipitate; solution of sugar of lead, a dirty yellow; protonitrate of mercury and pernitrate, a white; salts of copper, a brown precipitate, all of them decolorizing the liquid; nitrate of barytes, nitrate of lime and perchloride of iron do not cause any precipitate.

Gum and starch likewise afford with arsenic acid similar brown solutions. This is most distinct with inuline, from its not forming a paste. When the aqueous solution of inuline is heated for some length of time with arsenic acid, the inuline loses its property of separating on cooling, and on evaporation a rose-red mass is obtained, which gradually becomes black. The red colouring with arsenic acid is certainly peculiar to the fermentable sugars only; it has therefore the same power as other acids of effecting the conversion of gum, starch and inuline into fermentable sugar.—*Archiv der Pharm.*, xxxvii. p. 47.

Tests for Colouring Substances in Wines. By M. Jacob.

The author has found that basic acetate of lead on the one hand, and sulphate of alumina with carbonate of ammonia on the other, suffice for the detection and discrimination of the various colouring materials employed for colouring red wine:—

	Sulphate of alumina and carb. of ammonia.	Basic acetate of lead.
Ordinary red wine	Grayish precipitate	Bluish-gray precipitate.
Logwood	Dark violet precip.	Blue precip.
Brazil wood	Rose-red precip.	Wine-red precip.
Wild poppy	Grayish precip.	Dirty gray precip.
Recent juice of danewort (*Sambucus Ebulus*)	Bright violet precip.	Bluish-gray precip. Supernatant liquid violet
Fermented do.	Bright violet precip.	Beautiful grass-green precip.
Elder berries	Bluish-gray precip.	Dirty green precip.
Privet berries	Pale green precip.	Dirty green precip.
Litmus	Rose-red precip.	Bluish-gray precip.

When litmus is present in small quantity it is not indicated by the above tests; the wine should then be cautiously evaporated to the consistence of an extract, a small quantity of which is dissolved in a little distilled water, and then examined.—*Journ. de Chim. Med.*, 1844, p. 92.

Analysis of Alloys of Tin and Antimony.

Chevalier and Lassaigne have found that, on treating an alloy of these two metals with muriatic acid, none, or only very little antimonuretted hydrogen is given off, while the antimony separates as a black powder. If, on the contrary, the alloy is treated with nitric acid, the yellow insoluble mixture of oxide of tin and antimonious acid separated, ignited (when it becomes green), and treated with sulphuric acid and water, an abundant evolution of antimonuretted hydrogen gas takes place, which on ignition deposits large glittering films of antimony.—*Journ. de Chim. Med.*, 1844, p. 13.

CHEMICAL PREPARATIONS.

On the Preparation of the Hyposulphite and of the Trithionate of Potash. By* M. Plessy.

M. Langlois, to whom the discovery of trithionic acid is due, obtains it in combination with potash in the following manner:—He prepares some bisulphite of potash by passing sulphurous acid in excess into a solution of pure carbonate of potash. The salt thus obtained is introduced into a vessel containing pure flowers of sulphur, and the whole digested on a sand-bath, the temperature of which should not cause it to boil. Sulphurous acid is disengaged, and some sulphate is produced; the liquid assumes a yellow tint, which disappears at the end of two or three days, when the formation of the new compound is complete. The liquid, filtered whilst hot, becomes opake on cooling, and deposits some crystals, which are coated with a little sulphur. They are purified by dissolving them in a small quantity of warm water; the filtered solution no longer becomes opake, and furnishes very beautiful prismatic crystals.

When therefore sulphur is dissolved in the bisulphite, a liquid is obtained, which deposits a quantity of sulphur on boiling, and affords but a small quantity of the trithionate of potash and of an impure hyposulphite. The reaction does not take place in the manner first supposed; and although sulphurous acid is disengaged under the circumstances in which M. Langlois operated, we cannot have

$$KO\,(SO^2)^2 + S = KO\,S^2\,O^2 + SO^2.$$

* We have employed in this article the names suggested by Berzelius for the two new acids of sulphur (see this vol., p. 66), which have been generally adopted in Germany.

This evolution of sulphurous acid, observed by M. Langlois, does not always happen; thus it does not take place at 77° to 86°, and nevertheless the sulphur dissolves in the bisulphite. But if the bisulphate of potash is not adapted for the preparation of the hyposulphite, the neutral sulphite does perfectly well.

I will describe in a few words the process which I have adopted for preparing the hyposulphite of potash from the neutral sulphite. It may be of some service, as pure hyposulphite of soda may equally be obtained by it; and this is now a very important object of commerce.

Bisulphite of potash is prepared as above described; the carbonate of potash is wholly converted into bisulphite when the sulphurous acid passes off without dissolving. This is then converted into the neutral salt by adding carbonate of potash until it produces no further effervescence; the neutral sulphite, thus prepared, is boiled in a capsule or flask with flowers of sulphur, for fifteen or twenty minutes, stirring frequently with a glass rod to facilitate the solution of the sulphur. The liquid separated from the excess of sulphur is evaporated over the fire to a syrupy consistence; if any sulphate has formed in the course of the operation by the absorption of oxygen, a portion of the salt separates at this point of concentration. The clear liquid is decanted after 24 hours' standing, and again concentrated, which however does not determine the precipitation of a fresh quantity of sulphate, and in the course of 24 hours beautiful crystals of hyposulphite gradually form in a dry place.

The presence of the sulphate, far from being disadvantageous, causes the hyposulphite to crystallize better than from a pure concentrated solution. The crystals as obtained are perfectly colourless, transparent and hard, very soluble in water, not deliquescent, and contain 2 equiv. water of crystallization.

The hyposulphite of soda may be purified by melting it in its water of crystallization; on cooling, very beautiful crystals of hyposulphite separate, which are removed from the liquid containing the impurities.

I will now proceed to describe the process I employ for preparing the trithionate of potash.

I obtain this salt by the action of sulphurous acid on the hyposulphite of potash. This very remarkable action in some degree explains the formation of $S^3 O^5 KO$ by M. Langlois's process. In fact, it may be admitted that the sulphur, on dissolving in the bisulphite of potash, forms hyposulphite; and that the excess of sulphurous acid, instead of being disengaged, reacts upon this salt so as to produce the trithionate. This supposition, in fact, led me to examine the action of sulphurous acid on the hyposulphite of potash.

The following is the method I employ for the preparation of M. Langlois's salt:—

I procure a solution of hyposulphite of potash, so concentrated that it will not mix with alcohol of 0·851 spec. grav. When dry or crystallized hyposulphite of potash is conveyed into water to which

about $\frac{1}{8}$ volume of this alcohol has been added, the alcohol separates at a certain period, and comes to the surface. I add then no more salt, and pass through some sulphurous acid, generated from sulphuric acid and powdered charcoal; the solution of the hyposulphite is however previously heated to about 77° or 86°. If the disengagement of the gas is rather rapid, this temperature maintains itself. From time to time a little hyposulphite is added, taking care that the temperature always remains constant. When the liquid acquires an intense yellow colour, and gives off the smell of sulphurous acid, the disengagement of this gas is discontinued, and after some hours, in the course of the night, the liquor becomes colourless, quite loses the odour of sulphurous acid, and deposits a large quantity of crystals. The alcohol which floated on the surface now mixes with the liquid, which indicates that a fresh quantity of hyposulphite should be added and more sulphurous acid passed through if a greater quantity of crystals is desired.

When a sufficient quantity of these crystals has been obtained, they are dissolved in water at 122° or 140°, the solution filtered to separate the sulphur they contain, and then an eighth of its volume of alcohol of 0·851 spec. grav. added to the filtered liquor; it is again heated a little, and the solution furnishes on cooling perfectly pure, beautiful quadrilateral prisms. Their taste is slightly saline and bitter. On exposure to heat, they afford sulphurous acid, sulphur, and leave a residue of 64·36 neutral sulphate of potash; they are neutral, and dissolve readily in water. The aqueous solution is decomposed by sulphuric and nitric acids, with deposition of sulphur and disengagement of sulphurous acid. Hydrochloric acid does not decompose them; they do not give precipitates with solutions of lime, barytes, iron, zinc, magnesia, nickel, &c. They decolorize the red sulphate of manganese, but do not act on a solution of sulphate of copper; they precipitate the salts of protoxide of mercury black, those of the deutoxide blue, and give with the nitrate of silver a yellowish-white precipitate, which soon becomes black. The salt in question consequently possesses all the properties of the trithionate of potash.

The mother-ley of the crystals just described becomes turbid, and deposits sulphur when exposed to a temperature which would not decompose a solution of the trithionate of potash, and on adding some concentrated alcohol, deposits a salt in which crystals are perceptible, the form of which differs from that of the trithionate.

M. Gelis informs me that these crystals must be the tetrathionate, since this salt is likewise produced by the reaction of sulphurous acid on the hyposulphite.

When I became aware that M. Gelis was also investigating this reaction, I had only been able to determine approximately the quantity of sulphurous acid absorbed by a given weight of hyposulphite. I had observed, without however being certain of my results, that the absorption took place in the proportion of

$$2\,(S^2\,O^2\,KO) + 3\,(SO^2).$$

A deposit of sulphur is always formed when concentrated liquors

are acted upon. It became important to ascertain whether this deposit took place when dilute solutions were employed. I found that none forms in this case, and nevertheless there is absorption of sulphurous acid. MM. Gelis and Fordos have however analysed this reaction, and have been led to the following equation:—

$$2(S^2\,S^2\,KO) + 3(SO^2) = S^8\,O^5\,KO + S^4\,O^5\,KO.$$

The tetrathionate can be removed from the mother-ley from which the trithionate of potash was deposited. It is a white salt, not stable, but which keeps well enough in contact with the air when in the state of crystals and dry.

When the absorption of sulphurous acid by the hyposulphite of potash has determined the precipitation of a certain quantity of trithionate and of the tetrathionate of potash, some sulphate is found in the liquor. I have observed it form when access of air has been prevented; for when a recently prepared solution of sulphurous acid in boiled distilled water is passed under a bell-glass over mercury, and then a sufficient quantity of crystallized hyposulphite free from sulphate introduced, the sulphurous acid will be found to be completely absorbed after four-and-twenty hours, and the liquid affords a precipitate with chloride of barium, which does not dissolve entirely in dilute hydrochloric acid.—*Ann. de Chim. et de Phys.*, June 1844.

Pills of Extract of Aloes.

Extract of aloes readily absorbs moisture from the atmosphere, which renders it difficult to preserve in the form of pills. This inconvenience may be perfectly avoided, according to M. Röttscher, by adding a fourth part of carbonate of magnesia.—*Archiv der Pharm.*, xxvii. p. 335.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Source and Nature of Colouring Substances of Organic Origin, and on the Action of Oxygen upon them. By F. Preisser.

[Continued from p. 335.]

Carthamine.

It is to Beckemann*, Dufour† and Marchais‡ that we owe the knowledge of the chemical composition of the flowers of the *Carthamus tinctorius*, a species of thistle, better known by the name of *Safflower*. It is admitted that these flowers contain two distinct

* Beckemann, Société Royale de Gottingen, vol. iv. 1773, p. 96.

† Dufour, "Expériences et observations sur la composition chimique de la fleur de carthame."—*Ann. de Chimie*, vol. xlviii. p. 283.

‡ Marchais, "Observation sur le Mémoire de M. Dufour."—*Ann. de Chimie*, vol. l. p. 73, 1804.

colouring matters; one yellow, soluble in water, and which may be removed by simply washing; the other red, insoluble in water, soluble in weak alkalies, little soluble in alcohol, and still less in æther. M. Chevreul has given the name of *carthamine* to this latter. According to Döbereiner, the yellow matter is of an alkaline nature, whilst the red matter is so manifestly acid, that he proposed for it the name of *carthamic acid*. He states that this red principle forms peculiar salts with the alkalies, some of which, such as the carthamate of soda, crystallize in brilliant silky needles. These salts are all colourless, and offer the remarkable phænomenon of being precipitated, in the form of a brilliant rose-coloured substance, by vegetable acids*.

The best process for isolating carthamine is to exhaust the flowers with water, which removes the whole of the yellow principle. They are then placed in contact with water rendered slightly alkaline by a little carbonate of soda. The alkaline liquid is subsequently precipitated by hydrate of lead, which forms an insoluble lake of carthamate of lead. This salt, well-washed, is decomposed by an excess of sulphuretted hydrogen. It is filtered, and a light yellow coloured liquid, quite similar to the yellow principle obtained from the flowers by washing them with water, is thus procured. This liquid furnishes white acicular crystals by spontaneous evaporation, or immediately if sufficiently concentrated, which constitute pure *carthamine*.

Pure carthamine forms small white prismatic needles, of a slightly bitter taste. It is somewhat soluble in alcohol, but less so in water. Exposed to the air, it acquires a faint yellow colour. Sulphuric acid does not colour, but dissolves it; when concentrated, it blackens it in a few minutes. Hydrochloric and nitric acids produce no colour, and only dissolve it on the application of a gentle heat.

When introduced into a bell-glass full of mercury, with some bubbles of oxygen, it only acquires a yellow tint, even after several days; but in the presence of oxygen and alkalies it immediately undergoes a remarkable modification; it suddenly becomes yellow, then rose-red, analogous to the red of Carthamus. This substance then dissolves very readily in alkalies, and by neutralizing the solution with citric acid, red flakes, similar to the carthamine prepared by the ordinary processes, are deposited. We give the name of *carthameine* to this red matter.

Ammonia changes the white carthamine to a rose colour, with greater difficulty than caustic or carbonated potash or soda. When not in contact with the air, under a bell-glass full of mercury, the alkalies do not possess the property of transforming carthamine into *carthameine*. Acetate of lead precipitates carthamine in the state of white lake, which by lengthened contact with the atmosphere becomes yellow, and then rose colour. When thrown upon red-hot coals, carthamine melts, swells and decomposes, diffusing a pungent odour, but leaves no residue.

* Döbereiner, "Annales Générales des Sciences Physiques," Xe cahier, vol. iv.—*Journ. de Pharm.* vol. vi. p. 342, 1820.

Yellow Principle of the Safflower.—We at first considered the yellow principle of Carthamus as an intermediate state between white carthamine and carthameine; but upon examining its characters attentively, we have been obliged to alter our opinion. It was found impossible to obtain crystals from this yellow liquid; and by submitting it in a concentrated state to the action of chromic acid, peroxide of manganese and sulphuric acid, or to that of peroxide of lead, we were never able to restore its rose colour. Evaporated to dryness, this liquid afforded a yellow mass, which was treated with æther. The æthereal solution, after two days' spontaneous evaporation, deposited a pulverulent yellow matter, presenting merely indications of crystallization. This principle requires further examination, which want of time has not yet permitted us to undertake.

Analysis of Carthamine, of Carthameine and of modified Carthamine.—Pure carthamine afforded C 76·31, H 4·28, O 19·41, which corresponds to the formula $C^{26} H^{9} O^{5}$. The atomic weight = 2562·32. The crystals afforded 8·29 per cent. water; 2 atoms = 8·07.

Carthameine afforded—

	Found.	Equiv.		Calculated.
Carbon	70·50	26	= 1950·00	70·59
Hydrogen	4·08	9	112·32	4·06
Oxygen.....	25·42	7	700·00	25·35
			2762·32	

Modified carthameine afforded—

Carbon	69·28	24	= 1800·00	69·57
Hydrogen	3·44	7	87·36	3·38
Oxygen	27·28	7	700·00	27·05
			2587·36	

It is evident therefore that carthamine, on becoming coloured, absorbs 2 atoms of oxygen from the atmosphere, $C^{26} H^{9} O^{5} + O^{2} = C^{26} H^{9} O^{7}$; but under the influence of solar light and by lengthened contact with the air, it parts with 2 atoms carbon and 2 atoms hydrogen, which combine with 6 atoms oxygen, and are given off as carbonic acid and water, as is shown by the following equation:— $C^{26} H^{9} O^{7} + O^{6} = C^{24} H^{7} O^{7} + 2CO^{2} + 2HO$.

[To be continued.]

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

April 15, 1844. (W. T. Brande, Esq., Vice-President, in the Chair). The following communication was read:—

"An improved method for the Detection and Quantitative Deter-

mination of Arsenic in Cases of Poisoning," by Drs. R. Fresenius and von Babo.

The authors, after detailing the objections to the means at present adopted for detecting arsenic, as that of Reinsch, Marsh, and the various modifications which have been proposed of this latter method, gives the process which forms the subject of this communication. Part of the material to be tested is treated with hydrochloric acid, and chlorate of potash added, assisted by heat, and when sufficiently acted upon, filtered, and the solution concentrated; solution of sulphurous acid is next added in excess, and this excess afterwards expelled by heat. Sulphuretted hydrogen is then passed through the solution to saturation, ammonia added, and the whole lightly covered and kept warm until the odour of the gas has disappeared. The precipitate is collected on a filter, and is next acted upon by fuming nitric acid, added by degrees until the whole is moistened, and is then reduced to dryness in the water-bath. It is next moistened with hydrated sulphuric acid, and heated in a water-bath for two or three hours, and finally to about 302° Fahr. The dried and charred residue thus obtained is treated with from 10 to 20 parts of distilled water, hydrochloric acid added, and again precipitated as sulphuret, collected, and ammonia added, and the ammoniacal solution evaporated to dryness, and dried at 212°; the charred residue, and anything that remains undissolved by the ammonia, must be tested for lead, mercury, bismuth, copper, &c. The reduction of the resulting sulphuret of arsenic is then fully described, and the apparatus in which it is to be conducted figured. The process consists in mixing the sulphuret with dry carbonate of soda and cyanide of potassium, and introducing it into the reduction-tube, dry carbonic acid gas being passed over it, while it is gently warmed so as to expel all moisture; the flame of a spirit-lamp is applied to the tube beyond the materials, for the purpose of decomposing the liberated vapours, and another strong flame is gradually applied to the mixture until all arsenic is expelled. The reduced arsenic forms a film in advance of the first spirit-lamp flame; should zinc or antimony be present, they will be obtained in their metallic state by dissolving in water the residue found in the reduction-tube.

PATENT.

Patent granted to Claude Edward Deutsche, London, *for Improvements in combining Materials to be used for Cementing Purposes, and for preventing the Passage of Fluids, and also for forming or constructing Articles from such Compositions of Materials.*

The invention consists in a mode of treating bituminous substances, and combining them with other matters, so as to render them applicable to the various purposes now to be described.

The foundation of the invention is the use of combustible bitu-

minous substances, such as bitumen, asphalte, pisasphate, mattes, mineral caoutchouc, and the produce of the distillation of coal. To operate upon these matters, the patentee takes a certain quantity of bituminous substance (bitumen of Trinidad is preferred), and places the same in an ordinary distilling vessel; after closing it, heat is applied toit until the essential oil and water which is contained in the bitumen has been given off in vapour, which vapour will be condensed by its passing through an ordinary condenser, which is surrounded by cold water. When it has arrived at that stage that the condensed water, &c. comes away only in small drops, the bitumen under operation should be removed from the vessel, and passed through a metallic cloth sieve, arranged at the upper part of a basin containing water, and then the whole brought to a temperature of 122° Fahr. It may then be removed, and made into any form required.

Second Preparation.—Add to the matter above prepared from 1 to 50 per cent. of protoxide of lead, or of any other oxide, and mix them well together, by which an infusible substance is obtained, more or less so in proportion to the quantity of the metallic oxide that is put in.

Third Preparation.—Take a quantity of the material, prepared as described in the first preparation, and after having driven off by heat all the essential oil and humidity contained in it, then add from 1 to 20 per cent. of oil, reduced almost to a state of dryness by the addition of a quantity of litharge, or any other metallic oxide; then add a sufficient quantity of essential oil of turpentine, or other essential oil, until it is brought into the state or consistency of ordinary paint.

Fourth Preparation.—Add to a quantity of the first preparation a sufficient quantity of oil of turpentine, or other oil, to bring it to the consistency of ordinary paint.

Fifth Preparation.—Add to a quantity of the first preparation from 1 to 100 per cent. of fatty matters (the patentee prefers concrete whale oil), by which the fusibility of the substance will be more or less increased in proportion to the quantity of fatty matters that are put in. By adding to these different preparations a quantity of wax, gum resin, resin, sulphur or caoutchouc, a flexibility and adhesive property is obtained, more or less according to the quantity of such matters employed.

Sixth Preparation.—To make a brilliant black (brown) varnish, the bitumen should be well-heated until it is brought into a liquid state, and then passed through very fine heated sieves; then from 1 to 100 per cent. of gum resin or resin added, and the whole mixed well together, placed again on the fire, and left there until the whole of the essential oils and humidity have been evaporated, when spirits of wine, or essential oil of turpentine, or other oils, are to be added to bring it into the required consistency for use; ivory black, or other colouring matters, may then be added in a powdered state. If resin lac is used, it must be dissolved in alcohol, and added to the prepared bitumen, as explained in the fourth preparation. The bitumen, thus purified and mixed with

resin and resinous gums, will be found to be capable of being made into a very good sealing-wax.

Seventh Preparation.—Take a quantity of the first preparation, and add to it a quantity of either one, or several, vegetable products, such as caoutchouc, bdellium, copal resin, lac or elemi, or gum resin, or other resin, and add thereto a suitable quantity of any essential oil or alcohol, or even oil and alcohol mixed together. The adhesive nature of these preparations will be more or less increased in proportion to the quantity of gum resin which is put in. The first of these vegetable products, with the addition of a considerable quantity of oil or alcohol, may be usefully employed to render tissues, leather and wood impermeable. The last of these vegetable products, by the addition of a large quantity of resinous matter, will make a good cement for cementing stones, metals and wood used in the construction of vessels.

In preparing the matters for cementing purposes, the oil of naphtha (crude naphtha), obtained by distillation from bitumen, or coal mixed with a portion of alcohol, is the most preferable to be used, and the resin or gum resin that is preferred is the resin lac in sheets, as being of the most adhering nature.

The following is a list of preparations for cementing purposes, where the distilled bitumen may be added in quantities of from 1 to 100 per cent.:—

1st. Take 1 part of oil or alcohol and 2 parts of resin lac or any other resin, and melt them over the fire, keeping it well stirred up. For joining anything together, this is applied over the surface of the articles to be joined with a hard brush, taking care that all the surface is covered; heat is then applied until the cement is in a liquid state, when the articles to be joined together are placed one over the other and pressed together, and allowed to remain under pressure until the cement is cold.

2nd. Add 1 part of oil or alcohol with 1 part of bdellium, and melt them together over the fire; then add 1 part of resin lac or other resin, and heat it as before explained in No. 1.

3rd. Dissolve in water 1 part of gelatine and 1 part of oil or alcohol, with 1 part of resin lac; mix these products well together over the fire until they are well amalgamated, and then use them as explained in No. 1.

4th. Add to 1 part of bdellium 2 parts of gelatine dissolved in water, and 1 part of oil or alcohol, and heat them together until they are well mixed; then add 2 parts of resin lac dissolved in 1 part of alcohol, mix the whole together, and employ the preparation as explained in No. 1.

5th. Melt 2 parts of resin lac or other resin with 1 part of liquid styrax, and apply it as before.

6th. Melt 2 parts of resin lac in 1 part of turpentine, and apply it as before.

7th. Take 1 part of liquid styrax or turpentine, and add 4 parts of resin lac and 1 part of oil or alcohol, and mix the whole together, and apply it as before.

8th. Take 1 part of liquid styrax or turpentine, 1 part of alcohol and 2 parts of resin lac, and add to it 2 parts of gelatine dissolved in water, and mix the whole together, and apply it as before.

To all these preparations a proportion of caoutchouc may be added to the oils to give a flexibility to them, from 1 to 100 per cent., in proportion to the quantity of flexibility required.

The 1st, 2nd, 5th and 7th of the above-described preparations will be found more particularly applicable for caulking vessels that trade to those countries situated between the tropics; also in constructing of steam-boats it may be usefully applied to those parts which are near to the fireplace and boiler; also for stopping the cracks in the masts, yards and sides of ships; it may also be used as a cement for joining stone, wood and metals, for covering them in order to preserve them; also every description of linen, paper, leather, &c.; for making sealing-wax, and for forming subterraneous passages for water, for luting parts of steam-engines and chemical vessels; it may be formed into roofs, gutters and tubes of every description, for the passage of gas and other fluids; to form statues, vases, and other architectural ornaments. It may also be employed to preserve provisions, by coating the vessels containing them in such a manner as to exclude the atmospheric air.

The preparations described as the 3rd, 4th, 6th and 7th may be applied to painting purposes; they will be found particularly applicable to the preservation of steel, iron and other metals; for wood, linen, and any other description of article that may be exposed to damp.

The 5th preparation will be found particularly applicable to rendering leather impermeable; also for the caulking of ships.

With regard to this latter application, care must be taken in the preparation, that when the vessels go to hot climates there be a decreased quantity of fatty matters put therein, and a greater quantity when they go to cold climates.

The 1st, 2nd, 5th and 7th, when combined with the dust of stones, wood, coal, scoria, or the filings of metals or their oxides, may be employed to form walls, statues, vases, &c. &c.

In employing the 3rd, 4th, 6th and 7th preparations, varying the proportions as may be required, articles of linen, and waxed or varnish papers may be manufactured for the impermeability of leather, of linens, also for the preservation of wood, vegetable and mineral substances, and all matters which become injured by damp.

From the essential oils obtained in the distillation of the bitumen the naphtha contained therein is extracted, which has been for a long time employed for medicinal purposes; this naphtha will be very pure, and in quantities greater than those obtained from pitch.

To preserve substances from decay caused by worms and other insects, it will only be necessary to cover them over with a coating of any of the above products mixed with a portion of any poisonous matter, which will effectually prevent their ravages.—Sealed Oct. 8, 1842.

THE CHEMICAL GAZETTE.

No. XLIV.—August 15, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Examination of some Chlorates. *By* ALEX. WÆCHTER.

THE combinations of chloric acid with bases, with the sole exception of chlorate of potash, have never been submitted to so careful an examination as combinations of such an important acid seem to merit.

Chenevix presented to the Royal Society of London, in 1802, the first detailed investigation on this subject. He prepared the chlorates he describes by the action of gaseous chlorine on metallic oxides dissolved or suspended in water; he however obtained them in this way in such small quantity, and in so impure a state, that he himself does not vouch for the accuracy of the statements made with regard to their physical properties. He showed in his researches that certain compounds, such as corrosive sublimate and the metallic butters, &c., which were previously considered to be chlorates, were metallic chlorides. After M. Gay-Lussac had succeeded, in 1814, in preparing aqueous chloric acid in a pure state, Vauquelin repeated the investigations of Chenevix, and showed that the chlorates produced by the direct combination of the chloric acid with metallic oxides were identical with those which Chenevix had prepared in a different manner. As he obtained them by his process in a greater state of purity than his predecessor, he was able to rectify several errors relating to the properties of these salts; but he did not examine their composition, which is the object of the present investigation.

Chlorate of Soda.—NaO, ClO^5. The crystalline form of the chlorate of soda belongs to the regular system; it is generally a cube with tetrahedral surfaces. It dissolves in 3 parts cold and in less hot water, but only in a very small degree in alcohol; when heated it fuses at about the same temperature as the potash salt, giving off oxygen like it, and leaving behind a chloride of sodium, which has an alkaline reaction. It is anhydrous, and contains 29·31 per cent. soda.

Chlorate of Lithia.—LiO, ClO^5, HO. Carbonate of lithia was dissolved in pure aqueous chloric acid; the neutral liquor, evaporated over sulphuric acid, did not afford any distinct crystals, but solidified to a radiately crystalline mass. For the purpose of exami-

nation, this was pressed between warm blotting-paper, and then completely dried over sulphuric acid. Chlorate of lithia, obtained in this manner, forms a white, very deliquescent mass, which melts already at 122°, and at 284° begins to give off water, oxygen and some chlorine. When heated until all evolution of gas has ceased, the residue is chloride of lithium, which has an alkaline reaction; this salt, which contains 14·59 per cent. lithia, is very soluble in alcohol.

Chlorate of Ammonia.—NH^4O, ClO^5. Chlorate of barytes was decomposed with carbonate of ammonia; the filtered solution afforded, on evaporation over sulphuric acid, indistinct prismatic crystals, which were readily soluble in water, but scarcely at all in absolute alcohol. Vauquelin states that this salt is volatilized below the boiling point of water, but this assertion is founded on an error. It is suddenly decomposed at 216°, with a red flame. The products of the decomposition are watery vapour, nitrogen, chlorine, oxygen, muriatic acid gas and chloride of ammonium. Mixed with combustible substances, it detonates when struck just like the potash salt; it contains 74·25 per cent. chloric acid.

Chlorate of Barytes.—BaO, ClO^5, HO. This salt was prepared in large quantity, in order to obtain from it pure chloric acid and several chlorates, by saturating impure chloric acid obtained from chlorate of potash by means of fluosilicic acid with carbonate of barytes. It crystallizes, with evolution of light, in rhombic prisms. When heated it parts at 248° with its water of crystallization (5·88 per cent.), begins to give off oxygen at 482°, and fuses at 752°, giving off all the oxygen along with a trace of chlorine; if heated rapidly, it is decomposed suddenly and with detonation. Mixed with combustible bodies, it is decomposed like the potash salt when struck; it is slightly soluble in alcohol, and colours the flame green. The crystallized salt contains 46·53 per cent. barytes.

Chlorate of Strontia.—SrO, ClO^5. Carbonate of strontia was dissolved in chloric acid; the solution afforded, on evaporation over sulphuric acid to a syrupy consistence, large pyramidal crystals, which could not be measured from their rapidly becoming moist by exposure to the atmosphere. They are insoluble in alcohol; on being heated they decrepitate without giving off any water, and melt at nearly the same temperature as the barytes salt; when more strongly ignited they part with their oxygen and a trace of chlorine; the salt detonates like the potash salt, and contains 40·71 per cent. strontia.

Chlorate of Lime.—$CaO, ClO^5, 2HO$. A neutral solution of carbonate of lime in pure aqueous chloric acid afforded, on being evaporated to the consistence of a syrup over sulphuric acid, distinct crystals of chlorate of lime; they form oblique rhombic prisms with an oblique terminal surface, and deliquesce very quickly on exposure to the air. They dissolve readily in alcohol, and impart to its flame a beautiful red colour; when the crystals are heated rapidly to somewhat above 212°, they melt in their water of crystallization; but if the temperature be raised slowly, they lose their water of crystallization (14·10 per cent.) without melting; they are then an-

hydrous, and fuse at a temperature scarcely lower than the corresponding salts of barytes and strontia, give off like them oxygen and a trace of chlorine, and leave behind an alkaline chloride of calcium. They contain 23·36 per cent. lime.

Chlorate of Magnesia.—MgO, ClO^5, 6HO. The neutral solution of chlorate of magnesia, obtained by the decomposition of chlorate of barytes with sulphate of magnesia, afforded, on evaporation over sulphuric acid, only a laminar, crystalline, very deliquescent mass, which dissolved readily in alcohol. For examination, it was pressed between warm blotting-paper, and finally dried over sulphuric acid. It melts at 104°, and begins at about 248° to give off water, oxygen and chlorine. The residue, after prolonged heating, is a mixture of magnesia with chloride of magnesium; when heated very rapidly, it consists solely of magnesia. It contains 13·77 per cent. magnesia.

Chlorate of the Protoxide of Manganese.—The colourless solution which is obtained on decomposing chlorate of barytes with protosulphate of manganese, is decomposed on evaporation over sulphuric acid, at a certain degree of concentration, into chlorine, oxygen and hydrated peroxide of manganese. A dilute solution is not altered even on boiling. If some dilute sulphuric acid is added to it, it becomes intensely red by the formation of sulphate of the peroxide of manganese at the expense of the oxygen of the chloric acid. If some of the solution of the protochlorate of manganese is added to an excess of concentrated sulphuric acid, a brown crystalline precipitate forms, which is an intimate mixture of hyperoxide and protosulphate of manganese, which is insoluble in concentrated sulphuric acid.

Chlorate of the Protoxide of Iron.—A colourless neutral solution of this salt is obtained by decomposing a solution of the protosulphate of iron with chlorate of barytes; it soon however loses its neutrality, acquires a cinnamon colour, deposits basic perchlorate of iron, and leaves behind a deep red solution of perchlorate of iron mixed with perchloride.

Chlorate of the Protoxide of Tin.—Recently-precipitated hydrate of the protoxide of tin dissolves in aqueous chloric acid to a colourless liquid; this, however, was decomposed in a few minutes with violent detonations and an elevation of temperature, and formed at the end of the decomposition a gelatinous mass, which contained hydrated oxide of tin, perchloride of tin, and much free chloric acid.

Chlorate of Zinc.—ZnO, ClO^5, 6HO. The solution of chlorate of zinc was obtained by decomposition of chlorate of barytes with sulphate of zinc. It afforded, on evaporation over sulphuric acid, a crystalline, very deliquescent mass, which likewise readily dissolved in alcohol. Chlorate of zinc melts at 140°; at a somewhat higher temperature it parts with chlorine, oxygen and water, and leaves behind, when the heat has been sufficiently raised, pure oxide of zinc. It contains 23·72 per cent oxide of zinc.

Chlorate of Nickel.—NiO, ClO^5, 6H. A neutral solution of this salt, obtained by decomposing chlorate of barytes with sulphate of nickel, afforded, on evaporation over sulphuric acid, very beautiful

regular octahedrons of a dark green colour, which deliquesce very rapidly on exposure to the air, and dissolve readily in alcohol. They melt in their water of crystallization at 176°, and begin to be decomposed at 284° into chlorine and oxygen, with separation of water. If the temperature be not increased to above 392°, a black mixture of hyperoxide and chloride of nickel remains, which assumes a yellowish-gray colour at a faint red heat, and is then basic chloride of nickel. By long ignition this is converted into pure oxide of a silver-gray colour.

The salt contains 22·5 per cent. oxide of nickel.

Chlorate of Cobalt.—CoO, ClO^5, 6HO. Chlorate of barytes was decomposed with sulphate of cobalt; the solution filtered from the sulphate of barytes afforded on evaporation over sulphuric acid regular octahedrons, but in combination with the cube; the crystals are highly deliquescent, dissolve readily in alcohol, melt at 122°, are entirely decomposed at 212°, with evolution of chlorine, oxygen and water, leaving behind pure hyperoxide of cobalt. They contain 22·48 per cent. oxide of cobalt.

Chlorate of Copper.—CuO, ClO^5, 6HO. The solution of this salt, obtained by the decomposition of chlorate of barytes and sulphate of copper, afforded, on evaporation *in vacuo* over sulphuric acid, a dark green liquid of the consistence of a syrup, which did not solidify to a crystalline mass before being exposed to an intense degree of cold. Distinct crystals, which appeared to be regular octahedrons, were seldom obtained. Chlorate of copper is very deliquescent and readily soluble in alcohol; it melts at 149°, and is decomposed at a somewhat higher temperature. Melted chlorate of copper solidifies at a far lower temperature (68°) than its melting point (149°). When it is heated to 212° it gives off bubbles of gas, each of which causes a slight detonation. If the decomposition be effected at as low a temperature as possible, a green residue is obtained, which is only further decomposed at a temperature of 500°. It is insoluble in water, but dissolves readily in dilute acids; the solution in dilute nitric acid affords no precipitate with nitrate of silver; the solution in muriatic acid gives off a strong odour of chlorine. When heated strongly this compound parts with water, chlorine and oxygen, and leaves a pure oxide of copper free from chlorine. The green body is therefore a basic chlorate of copper, and contains water. The salt contained 23·45 per cent. CuO.

Chlorate of Lead.—PbO, ClO^5, HO. A neutral solution of this salt is obtained by saturating pure chloric acid with oxide of lead, which may be concentrated, without being decomposed, over a spirit-lamp, and crystallizes on cooling. The crystals are rhombic prisms. At first they are transparent and of great lustre, but they rapidly become dull and opake by exposure to the air. They do not deliquesce, dissolve however readily in water and in alcohol; mixed with combustible bodies, they detonate when struck with as much violence as the potash salt. At 302° they lose 4·59 per cent. water; at 446° they are suddenly decomposed, giving off chlorine and oxygen, while a black, partially fused mass remains behind, which

is a mixture of hyperoxide and chloride of lead, and which on further ignition is converted, with liberation of oxygen, into a yellow basic chloride of lead of constant composition. The salt contains 56·92 per cent. oxide of lead. The basic chloride of lead is PbO + 2PbCl.

Chlorate of Silver.—AgO ClO^5. A neutral solution is obtained on dissolving oxide of silver in pure chloric acid, which affords on evaporation very distinct prismatic crystals. Chlorate of silver is anhydrous, dissolves in about 5 parts cold water, and likewise in alcohol, without any change; it melts at 446°, and begins to give off oxygen, mixed with a trace of chlorine, at 518°. When heated until all evolution of gas has ceased, chloride of silver remains. It parts with its oxygen more quickly and readily when mixed with oxide of copper and manganese. When chlorate of silver is heated rapidly, it is decomposed at once with explosion and light. Mixed with combustible substances, it detonates when struck with greater violence than the potash salt. It contains 60·63 oxide of silver.

Chlorate of silver is likewise formed by passing chlorine through water in which oxide of silver is suspended, but it is again decomposed if chlorine gas be passed into it for too long a time; oxygen escapes, and chloride of silver and free chloric acid (no perchloric acid) are formed. By the action of hyperchlorous acid on oxide of silver, or on finely divided metallic silver, no chloric acid is formed, but a mixture of hyperoxide of silver and chloride of silver.

Chlorate of Silver and Ammonia.—AgO ClO^5, $2NH^3$. By dissolving chlorate of silver in ammonia and evaporating the solution, prismatic crystals of this salt, which are readily soluble in alcohol and water, are obtained. They melt at 212°, and give off their ammonia, so that when this temperature is not exceeded, pure chlorate of silver remains. Rapidly heated, it is decomposed with explosion and light; potash added to a solution of this salt gives a gray precipitate of Berthollet's fulminating silver.

Chlorate of the Protoxide of Mercury.—Hg^2 O, ClO^5. Recently-precipitated protoxide of mercury was dissolved in chloric acid; the solution, evaporated over sulphuric acid, afforded to the last drop beautiful prismatic crystals nearly an inch in length, which however rapidly lost their transparence and lustre by exposure to the air, and became dull. Water and alcohol dissolve the unaltered crystals readily and entirely, while those which have undergone some change leave behind a small white residue, which becomes black on boiling. A white precipitate is obtained on triturating the salt with water and chloride of sodium, and the supernatant liquid behaves neutral towards test-paper; the salt is therefore neutral chlorate of the protoxide of mercury. On exposure to heat it gives off oxygen at 482°, and is converted into a mixture of red oxide of mercury and corrosive sublimate, from which the latter may be removed by distillation at 563°, while the former remains behind if the temperature has not been allowed to exceed 698°. When heated rapidly, the decomposition takes place suddenly, and chlorine may be detected among the products of decomposition.

The insoluble modification of this salt, previously described by Vauquelin, was obtained by evaporating the solution of the salt to dryness in the water-bath, and extracting the residuous crystalline mass with water; it forms a white insoluble powder, which likewise afforded, on being triturated with chloride of sodium and water, a precipitate of calomel; it was therefore not a basic salt, and moreover it dissolved entirely in acetic acid. The whole of the mercury was precipitated as calomel by muriatic acid from the acetic solution. On being submitted to the action of heat, it afforded the same products of decomposition as the soluble crystallized salt. The acid liquid with which it had been edulcorated deposited on evaporation calomel in verrucous masses, and crystals of basic chlorate of peroxide of mercury. Mixed with combustible bodies, the protochlorate of mercury explodes with as much violence as the silver salt. It contains 73·63 Hg^2O, and 26·37 ClO^5.

Chlorate of the Peroxide of Mercury.—$2HgO, ClO^5, HO$. This salt was obtained in small tabular crystals by dissolving red oxide of mercury in chloric acid, and evaporating the solution over the water-bath. They are octahedrons, with predominant straight terminal surfaces. When heated, they first give off water, subsequently oxygen, and are then converted into a mixture of red oxide of mercury and corrosive sublimate, from which the latter may be removed by distillation at 563°. When heated rapidly, it is decomposed all of a sudden, and chlorine is then found among the products of decomposition. When mixed with combustible bodies, it generally inflames during the mixing, but without detonation. It is decomposed by water into a soluble acid and an insoluble basic salt. When triturated with chloride of sodium and a little water, an oxychloride of mercury separates with a red colour, and the supernatant liquid has a neutral reaction. The salt is therefore basic. It contains 72·13 per cent. peroxide of mercury and 24·91 chloric acid.

Chlorate of Cadmium.—$CdO, ClO^5, 2HO$. The solution of this salt obtained by precipitating chlorate of barytes with sulphate of cadmium, afforded on evaporation over sulphuric acid prismatic crystals, which were very deliquescent, and dissolved readily in alcohol. They melt at 176°, and give off water, oxygen and chlorine; the residue, if the temperature was sufficiently high, forms a gray fused mass, consisting of a mixture of oxide of cadmium with chloride of cadmium. On treating the residue with water, a portion of the chloride of cadmium is removed, while the other remains in combination with the oxide of cadmium, forming an insoluble white basic chloride of cadmium, in which however the chloride is so loosely combined with the oxide of cadmium, that it is converted, even by the carbonic acid of the atmosphere, into a mixture of carbonate of cadmium and chloride, from which the latter may be extracted by water. The salt contains 40·56 per cent. oxide of cadmium.

Chlorate of Bismuth.—The solution of oxide of bismuth in chloric acid is decomposed on concentration *in vacuo*, basic chloride of bismuth subsides, while hyperchlorous acid is disengaged.—*Journ. für Prakt. Chem.*, xxx. p. 321.

On the Occurrence of Xanthic Oxide in Guano.

Prof. Magnus recently communicated to the Berlin Academy of Sciences, that M. Unger had discovered in his laboratory Marcet's xanthic oxide in guano. This body, so highly interesting to physiologists and chemists, has hitherto occurred but twice as a diseased secretion in the form of a calculus. Liebig and Wöhler, in their researches on uric acid, have published the most complete description of it; they assign to it the name of *Urous Acid, Xanthine*; the quantity of the stone at their disposal was however exceedingly small.

Xanthic oxide is obtained from guano by extracting this substance with hydrochloric acid, and precipitating the solution with an alkali. Caustic potash then removes a small portion from the precipitate obtained, which however is not always equal in amount. Xanthic oxide is either precipitated from the solution in potash by a current of carbonic acid, or separated by the addition of chloride of ammonium, when it is deposited as the ammonia evaporates. The yellowish pulverulent body thus obtained has all the properties which Liebig and Wöhler assign to xanthic oxide; it differs only in this respect, that it is soluble in hydrochloric acid, as is evident from the mode of its preparation. But M. Unger has found that xanthic oxide not only enters into combination with hydrochloric acid, but likewise forms with several other acids crystalline compounds which are soluble in water, and the description of which he will soon publish in full.

Thus guano, so remarkable from its origin, and which promises to be of as great service for European agriculture as it has long been for certain districts of South America, likewise affords an interesting subject for science.

The small quantity of xanthic oxide which the guano contains does not admit of our supposing it to have originated by gradual decomposition; the occurrence of this body, known hitherto only as a diseased secretion of the animal organism, would afford a further proof, were it needed, that the guano consists, as shown by Alex. von Humboldt, of the excrements of animals. The inequality with which it is distributed in the guano renders it highly probable that it likewise has been secreted as a diseased product along with the excrements of the birds; otherwise we must admit that it forms the normal excrement of certain animals; in which case it would be of great interest to become acquainted with these species of animals, which perhaps may still exist.—Poggendorff's *Annalen*, No. V. 1844.

Coumarine in Asperula odorata.

M. Kormann has found that this plant does not derive its agreeable odour from one of the ordinary essential oils; for on distillation with water and sulphate of soda the distillate contained not a trace of essential oil, and possessed only an herbaceous smell. On exhausting the plant with alcohol, treating the extract with æther, evaporation of the æthereal extract, and digesting the residue with boiling water, there is obtained, on the cooling of this aqueous de-

coction, a warty crystalline substance, possessing all the properties of coumarine. The green residue is likewise a mixture of chlorophylle and coumarine, from which the latter may be obtained by sublimation.—*Journ. de Pharm.* for May 1844.

On the Action of Boracic Acid upon Alcohol and Pyroxylic Spirit. *By* M. Ebelmen.

On examining the method employed by Gmelin to determine the quantity of boracic acid in siliceous minerals, I found that alcohol, distilled over boracic acid, carried with it a much larger proportion of this body than pure water. This fact, altogether inexplicable on admitting that the boracic acid is carried over by the vapours of water and alcohol, owing to the tension of its vapour at the boiling-points of these two liquids, led me to examine whether in the distillation of alcohol over boracic acid a combination was not formed between the elements of the two bodies. I soon found that it was possible to produce under these circumstances a true boracic æther. The following was the method adopted for the preparation of this compound:—

When equal weights of absolute alcohol and of fused pulverized boracic acid are mixed, a considerable evolution of heat soon results. On endeavouring to expel the alcohol by distillation, it was found that the temperature might rise, in the interior of the retort, far above the boiling-point of alcohol before the whole of the liquid disappeared. On discontinuing the distillation at 230°, then treating the cold mass with anhydrous æther, decanting the æthereal solution, and gradually heating it in the oil-bath to 392°, a residue is obtained consisting of a slightly viscid liquid, which affords on exposure to the air at this temperature abundant white vapours, which solidify on cooling.

This compound, which I consider to be boracic æther, approaches considerably by its physical properties to boracic acid and the metallic borates, which, as is well known, assume the vitreous state on being melted. It forms a transparent glass, but one which is somewhat soft at the ordinary temperature, and which can be drawn out into very thin threads, between 104° and 122°; it has a weak æthereal odour and a burning taste. Placed on the skin, it produces a very decided impression of heat, and is soon converted into a white powder of boracic acid. It likewise bleaches by exposure to the air, but this alteration is only superficial with fragments of a certain size.

It is decomposed at about 572°, producing an abundant disengagement of a gas which presents all the characters of olefiant gas. This gas burns with a green flame, which arises from its always carrying with it a certain quantity of undecomposed boracic æther; but the addition of a little water deprives it of this property.

This mode of decomposition of boracic æther forms a ready method of preparing olefiant gas. On heating a mixture of 3 parts of fused boracic acid and 1 part absolute alcohol in a flask, an

abundant and regular evolution of olefiant gas is produced without the mass becoming carbonified. Monohydrated boracic acid, which is formed in this decomposition of the alcohol, does not part with its water except at a very high temperature. Triturated in warm water, boracic æther decomposes, with a considerable evolution of heat, into boracic acid and alcohol. It dissolves in every proportion in alcohol and æther; water solidifies these solutions.

When an alcoholic solution of boracic acid is distilled, the alcohol carries over with it a considerable quantity of this body, which imparts to it the property of burning with a green flame and of becoming opake in water.

The results of the analysis which I made of this body nearly correspond to the formula $Bo^6 C^4 H^5 O$. The composition of this body will allow of our determining the true equivalent of boracic acid, showing that borax, $Bo^6 NaO$, is a neutral salt.

The action of boracic acid on pyroxylic spirit is quite analogous to that which it exercises on alcohol, but I have not yet isolated and examined the product which is formed; I have also begun some experiments, with a view of producing borovinates and some boromethilates; but they are not sufficiently advanced for publication. —*Comptes Rendus*, June 24, 1844.

On Maleic Acid, the Preparation, Properties and Composition of its most important Salts. *By* P. Buchner, Jun.

Maleic acid is, as is well known, a product of the decomposition of malic acid at a high temperature. The more rapid the distillation of the hydrated malic acid is effected, the greater the quantity of maleic acid obtained; and M. Liebig has moreover found that the product is far more considerable on employing a large retort and receiver in this operation. The acid is thus obtained in transparent, colourless, oblique rhombic prisms; it effloresces on the sides of the vessels by spontaneous evaporation of the aqueous solution; it is very soluble in water, alcohol and æther; the aqueous solution has a very acid taste, which is subsequently acrid, styptic and metallic; it strongly reddens litmus-paper.

The crystals contain 1 atom of water, which is expelled by heat, and then the acid is easily decomposed.

The principal character of the hydrate of maleic acid, that which distinguishes it from the hydrate of aconitic acid, with which it is isomeric, is its behaviour towards heat. The hydrate of maleic acid, when submitted to distillation, is decomposed into water and into a white volatile substance, which fuses at 133° and boils at 349°, and possesses the composition of anhydrous maleic acid. This substance, heated above its boiling-point, is decomposed, and becomes brown, giving off inflammable gases and leaving a carbonaceous residue.

If the hydrate of maleic acid be kept in fusion for some time, it presents perfectly similar phænomena to those of the hydrate of malic acid; the liquid mass is gradually converted into a solid

crystalline paste of pure hydrate of fumaric acid, from which it is easy to separate any undecomposed maleic acid by washing with water.

The hydrate, as well as the anhydrous maleic acid, have been analysed by Pelouze and Liebig; the latter consists in 100 parts of 49·45 carbon, 2·02 hydrogen, and 48·53 oxygen = C^4HO^3. Its atomic weight = 618·323, and its combining proportion = 16·14. It is a bibasic acid. The formula of the hydrate should therefore be doubled; it must consequently be expressed by $C^8H^2O^6 + 2HO$.

A bibasic acid forms, as is well known, two series of salts; in the one, 2 atoms of hydrate water are replaced by 2 atoms of metallic oxide, which constitutes the series of bibasic or neutral salts; in the other, only 1 atom of hydrate water is replaced by 1 equiv. of metallic oxide, forming the series of monobasic or acid salts.

Formula of the neutral salts ..... $R + 2MO$

Formula of the acid salts ..... $R + \begin{cases} HO \\ MO \end{cases}$

One of the principal characters of a bibasic acid, and which distinguishes it essentially from monobasic acids, is its property of forming acid salts with lime, barytes and oxide of silver—a character which malic acid possesses.

The neutral salts which this acid forms with the alkalies do not crystallize; they are very soluble in water and in alcohol. The salts of ammonia and potash are strongly hygroscopic; they combine with the hydrate of the acid to form acid salts, which are very soluble in water and crystallize. The maleates of potash and of soda form together a double salt.

Maleic acid likewise affords easily crystalline acid and neutral salts with the alkaline earths. The neutral salts of the earths do not form double salts either with each other or with the neutral salts of the alkalies.

The author then passes in review each of the most important salts of maleic acid, and indicates the formulæ at which he has arrived. We shall only enumerate the principal:—

Neutral maleate of potash	$C^8H^2O^6$, 2KO.
Acid maleate of potash	$C^8H^2O^6$, KO, HO + HO.
Neutral maleate of soda.....	$C^8H^2O^6$, 2NaO + HO.
Acid maleate of soda.....	$C^8H^2O^6$, NaO, HO + 6HO.
Maleate of potash and soda ..	$C^8H^2O^6$, NaO, KO.
Neutral maleate of barytes ..	$C^8H^2O^6$, 2BaO + 2HO.
Acid maleate of barytes	$C^8H^2O^6$, BaO, HO.
Neutral maleate of silver	$C^8H^2O^6$, 2AgO.
Acid maleate of silver	$C^8H^2O^6$, AgO, HO.

If we direct our attention to the constitution of the compounds analysed by the author, maleic acid will be found to possess all the characters of a bibasic acid. Now although the essential characters of a bibasic acid consist in the 2 atoms of hydrate water of the hydrated acid being susceptible of replacement by bases in the neutral salts, the bibasic maleates exhibit an anomaly in this respect,

which is that the 2 atoms of hydrate water, which are not expelled at 212°, still occur in them almost without exception. It differs in this respect from tartaric acid, for in the neutral salts of this latter there is complete absence of hydrate water. M. Buchner inclines to the opinion that the hydrate water in the neutral maleates indicates that it is susceptible of being replaced by other neutral metallic maleates, and that in this manner several kinds of double salts may be formed; for instance, maleates of copper and potash, of nickel and potash, of zinc and potash, &c.—Liebig's *Annalen*, vol. xlix. p. 57.

On the Action of Nitric Acid on Butyrone. *By* M. Chancel.

When a mixture is made of equal volumes of nitric acid of ordinary strength and of butyrone, the latter collects on the surface, acquiring a strong red colour. On exposing the flask containing the mixture to a moderate heat, a lively reaction suddenly ensues, after a few minutes; red vapours are disengaged in abundance, and would throw some of the liquid out of the apparatus were it not immediately removed from the fire. The apparatus should be so arranged that the red vapours pass through a vessel containing water, on the surface of which a volatile liquid collects, of a somewhat agreeable æthereal odour, which has some analogy with that of butyric æther. As soon as the evolution of red vapours has ceased, the liquid in the flask is poured into a large quantity of water, when a nitrogenous acid subsides in the form of an oily liquid, which is purified by repeated washings. This acid and the æthereal liquid above mentioned are the only two substances that are formed at the expense of the butyrone; in this reaction merely traces of carbonic acid are disengaged.

Butyronitric Acid.—This is an oily liquid, strongly coloured yellow, which does not congeal in a mixture of solid carbonic acid and æther; it possesses an aromatic odour and a very decided sweet taste. It easily ignites, and burns with a reddish flame; it is insoluble in water and soluble in alcohol in every proportion; its density is greater than that of water. The properties which I have just noticed are common to butyronitric acid, obtained directly from the action of nitric acid on butyrone and that from the salt of potash. This acid easily combines with bases, and affords crystallizable salts.

From the comparison of a great number of analyses made with the free acid and combined with bases, the result is that butyronitric acid is a bibasic acid, containing in a free state 2 equiv. of water, susceptible of being wholly or in part replaced by bases.

The formulæ which express the composition of butyronitric acid and of some butyronitrates are—

Free acid ..... $C^7 H^6 O, NO^4 + 2HO.$

Salt of potash ..... $C^7 H^6 O, NO^4 + \left\{ \begin{matrix} KO. \\ HO. \end{matrix} \right.$

Neutral salt of silver ..... $C^7 H^6 O, NO^4 + 2AgO.$

Acid salt of silver ..... $C^7 H^6 O, NO^4 + \left\{ \begin{matrix} AgO. \\ HO. \end{matrix} \right.$

Salt of lead..... $C^7 H^6 O, NO^4 + 2PbO.$

On examining these formulæ, we observe that an equivalent of hydrogen has been eliminated from the butyrone and replaced by an equivalent of hyponitric acid, a circumstance which happens with many organic substances when submitted to the action of nitric acid.

Butyronitrates.—By mixing an alcoholic solution of potash with some butyronitric acid, the liquor becomes slightly coloured; numerous crystals then appear, which at last form a paste; these crystals are collected, and purified by washing with alcohol. When obtained in this manner, the butyronate of potash presents itself in the form of small laminæ of a beautiful yellow, which calls to mind that of iodoform. At a temperature of about 212° it ignites with a kind of explosion; this property is common to all the butyronates which I have examined. This salt of potash is nearly insoluble in alcohol; it dissolves in about 20 times its weight of water; its aqueous solution precipitates salts of silver and of lead yellow, and salts of copper of a dirty green colour.

When a solution of butyronitrate of potash is treated with nitrate of silver, a precipitate of butyronitrate of silver with 2 equiv. of base is formed; this salt, at first yellow, becomes rapidly of a violet colour. It is soluble in a large quantity of water, and crystallizes by spontaneous evaporation. The aqueous solution of this salt at the boiling temperature presents a somewhat remarkable reaction; 1 equiv. of base is precipitated, and replaced by 1 equiv. of water; so that a salt, of analogous composition to the salt of potash, crystallizes from the filtered liquor.

Chlorobutyrine.

On distilling butyrone with perchloride of phosphorus, it is immediately attacked, phosphoric acid is formed, and there is a disengagement of hydrochloric acid; the liquid which distils over possesses a peculiar odour, and contains considerable quantities of chlorine. However, to obtain a definite product, it is requisite to redistil the liquid several times with perchloride of phosphorus, since the last traces of butyrone are acted upon with difficulty. It is purified like the compound æthers.

It forms a colourless limpid liquid, lighter than water, in which it is insoluble; it dissolves in every proportion in alcohol; it possesses a peculiar penetrating odour, is inflammable, and burns with a flame the borders of which are green, and boils at 320°. Nitrate of silver produces no opalescence in its alcoholic solution; but if, after ignition, this test is added to the residue of the combustion, considerable quantities of chlorine are evidenced by an abundant precipitate of chloride of silver. Its composition is represented by the following formula, $C^{14} H^{13} Cl$, which represents 4 volumes of vapour. Nevertheless, experiment gives a little more carbon and

less chlorine than the formula requires, which should probably be attributed to the presence of a small quantity of unaltered butyrone. —*Comptes Rendus*, June 3, 1844.

ANALYTICAL CHEMISTRY.

New Method of detecting the Presence of Sugar in Diabetic Urine. *By* Dr. Cappezuoli.

This author does not use the blue solution adopted by Frommchers and Taddei (a compound of albumen, potash and oxide of copper), but a few grains of hydrated oxide of copper and a solution of caustic potash in sufficient quantity to render the liquid distinctly alkaline. The operation takes place at ordinary temperatures. The urine is obtained fresh, placed in a cylindrical vessel, either conical or straight, the copper and potash then added, the mixture shaken, and then laid aside. It becomes troubled from the precipitation of the phosphates which were dissolved in it, and from the oxide of copper which it contains in suspension. It gradually however becomes clear, in consequence of the subsidence of a voluminous deposit, which is at first of a sky-blue colour, but at the end of a few hours a canary-yellow circle is perceived to form upon its surface, and usually to pervade the whole mass; subsequently a red colour, more or less deep, in the form of a zone, replaces the yellow, either wholly or in part. This phænomenon, which takes place in 24 hours, is owing to the reaction of the sugar on the oxide of copper. In fact, this base is gradually deprived of its oxygen until the metal is reduced. The sugar, by absorbing oxygen, is transformed principally into formic acid, which combines with the potash. The reaction is rapid when grape-sugar is used, such as that of diabetes. The yellow zone, and the red one which succeeds it, are true characteristics of the presence of sugar in diabetic urine; for they are not produced in the normal state, nor in any other diseased condition of the urine. It might be feared that the presence of sugar of milk, in certain urines, might cause the same appearances, because, as is well known, it approaches very nearly to grape-sugar; but such does not occur save when the milk-sugar is in very considerable quantity, and then it requires a much longer time. The same hold good with urines containing the volatile oils of turpentine, copaiba, &c. The author, in acting upon urines to which an addition of honey or grape-sugar has been made, has constantly obtained the red zone, nearly always preceded by the canary-yellow colour. The rapidity with which the reaction occurs, and the brightness of the tints, depend either on the more or less complex composition of the urine or excess of potash or sugar. Moreover, when the phænomenon is not produced within 24 hours, the addition of a little potash causes it to appear.—*Journ. de Pharm.*, Juillet 1844, from *Gaz. Toscane.*

Preparation of a pure Mixture of Carbonate of Potash and Carbonate of Soda.

Du Menil recommends preparing the mixture of equal atoms of carbonate of potash and carbonate of soda, so frequently employed in analysis for decomposing silicates, by reducing Rochelle salt to ash in a sufficiently capacious crucible, extracting the mass with water, and evaporating the filtered solution to dryness.—*Archiv der Pharm.*, xxxv. p. 17.

PHARMACOLOGY.

Observations on Balsam. Copaivæ. By J. E. Simon.

The genuineness of copaiva balsam is frequently tested by mixing 3 parts of balsam with 1 of caustic ammonia of 0·96 spec. grav. If the mixture is rendered clear by shaking, the balsam is usually considered genuine. If to this balsam the sixth part oil of juniper-wood be added, it behaves towards ammonia precisely like the genuine, likewise affording a clear combination, which proves the insufficiency of this test.

Of late there has frequently occurred in commerce a balsam which will not at all bear the above test with ammonia. I have taken much trouble to detect any adulteration in this balsam, but am thoroughly convinced that it is perfectly genuine. It contains from 20 to 25 per cent. more essential oil, which renders it more liquid, but the oils from both kinds of balsam are identical in odour and in all other properties; the residuous resin in both kinds becomes equally hard and brittle, which entirely does away with the supposition of its having been adulterated with any fat oil; the two resins however differ, the one affording a soapy combination with caustic alkalies, which the resin of the new balsam does not.

Whether this new balsam is obtained from younger trees, or whether it is derived from a different species; whether the one is more active than the other, it is impossible for me to say; but the latter is decidedly not adulterated, for on boiling with water not the least foreign odour is perceptible, and the residue, after boiling and driving off the volatile oil, is hard and brittle like sealing-wax.—*Archiv der Pharm.*, May 1844.

Analysis of Galls. By M. Guibourt.

Galls contain, according to the author, the following constituents which pre-exist in them:—

Water, 11·5; woody fibre, 10·5; tannine, 65; gallic acid, 2. Ellagic acid and luteo-gallic acid, 2. Brown extractive substance, 2·5. Gum, 2·5. Starch, 2. Chlorophylle and volatile oil, 0·7; sugar, 1·3; albumen and salts.

The author assigns the name of luteo-gallic acid to the yellow colouring principle of the galls. It may be separated from ellagic acid by dissolving the two in potash and exposing the solution to the atmosphere; ellagate of potash is deposited in proportion as carbonic acid is absorbed from the air, while the luteo-gallate of potash remains in solution.—*Ann. der Chem. und Pharm.*, xlviii. p. 359.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Source and Nature of Colouring Substances of Organic Origin, and on the Action of Oxygen upon them. By F. Preisser.

[Continued from p. 352.]

Santaline.

Pelletier analysed Red Saunders wood in 1834, and isolated the red colouring principle, which he designated by the name of *Santaline**. In 1832 he submitted this substance to elementary analysis, and represented it by the formula $C^{16} H^{8} O^{32}$. He considered it as an acid from its affinity for bases. In his treatise he observes that "the solution of santaline in sulphuric æther is not instantaneous; it only takes place after long contact, and the solution, instead of being red as in alcohol, is of an orange colour, and even yellow if access of air be prevented. By the spontaneous evaporation of the æther in the open air, the colouring matter is obtained of a superb red. If the æther is quickly evaporated *in vacuo*, the colour is much less intense; it is even frequently quite yellow. It is also remarkable that, however anhydrous the æther employed may be, and although the santaline may have been perfectly dried, water always remains after evaporation of the æthereal dye. It frequently happens that ice is formed when the evaporation is effected rapidly under the bell-glass of the air-pump. How can we explain these phænomena? We should be tempted to believe that santaline, on dissolving in the æther, loses a portion of its oxygen, that water is formed at the expense of the hydrogen of the æther, and that subsequently the santaline by exposure to the air again recovers all the intensity in its colour by absorbing oxygen. This explanation requires however to be supported by facts†."

Extraction and Characters of the Santaline.—Saunders wood is treated with æther, which becomes strongly coloured dark red. The liquid, evaporated to two-thirds, is mixed with hydrate of lead; when an abundant dark red lake (santalate of lead) is formed. This salt, washed on a filter, then suspended in water, is submitted to a current of sulphuretted hydrogen, and filtered, when a liquid is ob-

* Pelletier, "Du Santal rouge et de sa Matière colorante."—*Bulletin de Pharmacie*, vol. vi. p. 484, 1814.

† Pelletier, *loc. cit.*, p. 193.

tained which is faintly yellow. By evaporation *in vacuo* it furnishes a whitish crystalline powder, which is pure *santaline.*

This powder easily absorbs oxygen from the air. When it is boiled with water, it becomes red. The alkalies, potash, soda and ammonia, give it a dark red colour instantaneously. Acetic, nitric, hydrochloric and sulphuric acids, in a dilute state, dissolve and turn it red.

It combines with oxide of lead; the salt is of a brown red colour. It is soluble in water, alcohol and æther. The solutions become red at the edges. A drop of alkali darkens the tint immediately.

Santaline in solution, submitted to ebullition, deposits a red powder on cooling, in which a quantity of small needles of a bright red colour are perceptible by means of a microscope. This is *santaleine.* When ignited in a tube, it affords no nitrogenous product.

[To be continued.]

Formula for Red Ink. By M. Heusler.

2 oz. of the best Brazil wood, $\frac{1}{2}$ oz. pounded alum and $\frac{1}{2}$ oz. crystals of tartar are boiled with 16 oz. of rain or distilled water down to half; $\frac{1}{2}$ oz. of gum-arabic is dissolved in the strained liquid, and finally a tincture, made of $1\frac{1}{2}$ drachm of cochineal and $1\frac{1}{2}$ oz. of alcohol of 0·839 spec. grav. mixed with it.—*Jahrb. für Prakt. Pharm.*, viii. p. 368.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

May 6th, 1844. (Thomas Graham, Vice-President, in the Chair.) The following communications were read:—

"On the Composition of some Varieties of South American Guano, with a Description of a new Mode of estimating Ammonia, and of a Process for separating Lime from Magnesia when in combination with Phosphoric Acid," by Mr. J. D. Smith.

Mr. J. D. Smith describes the several varieties of South American guano which he analysed. He divides them into three kinds—the pulverulent, the concrete and the saline, and dwells particularly upon their different composition; and by comparing the result of the analyses, draws attention to the abundance of urate of ammonia in one kind, and its nearly total absence in another; the quantity of potash and soda salts contained in the saline guano, and the very large quantity of phosphate of lime contained in the concrete guano; also noticing the variation in the quantity of ammonia contained in each; and then remarks that we can hardly wonder that such widely differing results should have been obtained by various farmers and experimentalists, even when the application of these various guanos have taken place under almost identical circumstances as respects the quality of land, description of crops, time of application, &c. It is obvious that the effect of such manures must vary almost as

widely as their composition, and that whilst the employment of such guano as Nos. I. and II. would be attended with successful results, the use of others might in some cases, and especially such as No. VII., prove absolutely detrimental to the crops.

The method of analysis of each sample of guano is detailed at length, Mr. Smith recommending a mode of ascertaining the amount of ammonia contained in guano, by distilling it over with carbonate of soda, with certain precautionary measures, and then precipitating the carbonate of ammonia thus obtained by nitrate of barytes, and calculating the ammonia by the weight of carbonate of barytes. The separation of phosphate of lime from phosphate of magnesia was effected by acetic acid; it depends upon the different solubility of these two phosphates in this acid.

Mr. Smith divides the guano to be analysed into three parts, viz. into the portion soluble in cold water, that soluble in boiling water, and into the insoluble in either, and gives the analysis of each. The following is a mere summary of the result of Mr. Smith's analysis, serving in some measure to show the variety of composition existing between them:—

	I.	II.	V.	VI.	VII.
Water	22·20	25·75	25·00	18·73	7·07
Volatile salts	36·86	19·50	15·50	4·24	5·00
Organic matter	7·13	10·00	2·30	0·40	3·00
Fixed alkaline salts....	8·10	8·75	36·70	3·67	67·00
Phosphate of lime, &c.	25·10	33·50	19·00	71·00	16·00
Sand, &c.	1·00	1·60	0·70	2·00	0·04
Containing of ammonia	6·68	6·43	5·08	0·14	0·97

Mr. Smith then alludes to the formation of oxalate of ammonia, and states that he is compelled to differ on this point from the theory brought forward by Dr. Fownes. Mr. Smith advances an hypothesis for its mode of production, by the absorption of water and very slight oxidation, and the conversion of the urate into oxalate of ammonia without the formation of carbonate of ammonia, or any other secondary products. Mr. Smith concludes by remarking, that he never held but one opinion—that this manure is deposited by sea-fowl inhabiting the coasts where no rain falls, and which consequently is never washed away, and rejects the idea of its being a coprolite.

"Observations on the Decomposition of the double Cyanides by the Electric Current," by Mr. James Napier.

From the value of the double cyanide of silver and potassium in the operations of electro-metallurgy, the author's attention was first directed to the study of that substance.

It has been observed, that when a solution of the pure salt is employed, decomposition is very difficult, unless the battery be of very considerable power; but the addition of a slight excess of cyanide of potassium greatly facilitates the operation, and renders a much weaker voltaic arrangement fully sufficient for the purpose. This effect has been commonly ascribed to an increase of conducting

power conferred by the alkaline salt, and even to a kind of "disposing influence" imparted by that substance to the solution. Mr. Napier has shown experimentally, that in all probability the retardation of the current is due to the formation of a crust of cyanide of silver on the positive electrode, when the latter is of silver; when an excess of cyanide of potassium is present, the crust so produced is immediately dissolved off, and the current passes without interruption; if a positive electrode of platinum be employed, nothing of the kind happens, and the action proceeds perfectly well with the pure salt.

It appears from the author's experiments, that when the electrical force employed in the decomposition of the salt in question is not too great, but is judiciously apportioned to the work to be executed, it is the cyanide of silver alone which undergoes decomposition, the cyanide of potassium being merely set free; but when, on the other hand, the power is excessive, the last-named substance is also decomposed, and hydrogen is evolved at the negative pole.

When a solution of the double cyanide is electrolysed, platinum plates being used, if the current be weak, the cyanogen evolved at the positive side is absorbed by the solution, turning it dark brown. If the current be strong, oxygen gas is evolved from the positive pole, the cyanogen being decomposed, and cyanide of silver deposited upon the metal.

Although the double cyanide is certainly, when in solution, an excellent conductor for electricity, and decomposed with great ease when the accumulation of insoluble cyanide upon the electrode is prevented, it is remarkable that the proneness to decomposition is very much increased by a further addition of cyanide of potassium. When an additional equivalent of that substance is added, the solution is more easily decomposed than that of any substance known, one square inch of copper and zinc immersed in water sufficing.

The author concludes with some remarkable experiments, illustrative of the manner in which the elements of an electrolyte are transmitted from particle to particle across the fluid interposed between the electrodes.

"On the Occurrence of Mannite in the *Laminaria saccharina*, and other Sea-weeds," by John Stenhouse, Ph.D.

After reviewing the experiments and published reports of various authors, Dr. Stenhouse proceeds to detail the examination of a great variety of sea-weeds; out of eight different species examined, mannite was separated, and in the case of the *Laminaria saccharina* amounting to 12·15 per cent. The method of separation consisted in digesting the dried extract by hot water, with boiling alcohol, and allowing the mannite to crystallize out by cooling; as thus obtained its composition was $C^6 H^7 O^8$. Mannite may be distinguished from cane-sugar by its not being discoloured from the action of strong sulphuric acid and a gentle heat; and from grape-sugar by boiling with strong solution of caustic potash or soda, the mannite dissolving without change of colour. When heated with solution of potash and sulphate of copper, it does not precipitate the red oxide of copper, as is the case with grape-sugar.

Dr. Stenhouse could not detect mannite in the Couch-grass, as stated by Prof. Pfaff, but obtained crystals of binoxalate of potash, which appear to have been mistaken for the former substance.

"On Fluorine in Recent and Fossil Bones, and the Sources from whence it is derived," by J. Middleton, Esq.

The author found fluorine in the organic remains of the *Carnivora*, *Herbivora*, *Reptilia* and *Pisces*, and in the recent bones of man and reptiles; and considers that this increases in quantity in fossil bones in proportion to the remoteness of the period at which they lived. These facts taken conjointly, Mr. Middleton argues, seemed to need some more general source for fluorine than has been hitherto offered; and he was, in consequence, induced to examine ordinary water as the vehicle by which the accumulation might be effected. Various calcareous and mineral deposits of aqueous origin were therefore examined for fluorine, and with only one exception that body was found to be present. It follows as a corollary, that it exists in most, if not all vegetables, though perhaps in quantities too small for detection.

PATENT.

Patent granted to James Napier, Hoxton, Middlesex, *for Improvements in preparing or treating Fabrics made of fibrous Materials, for covering Roofs, and the Bottoms of Ships and Vessels, and other Surfaces, and for other Uses.*

This invention consists in coating or incorporating with metal, by electric deposition, fabrics made of fibrous materials, such as linen, canvas, woollen, silk, calico, cord, thread, rope, paper, pasteboard, felt, &c. The patentee does not confine himself to any particular mode of conducting the process; but he describes some methods which he has employed, dividing his description into two parts, viz. the preparation of the fabric to give it a conducting surface, and the deposition of metal thereon by electricity.

In the preparation of the fabric, the patentee employs any of the well-known methods of reducing the metal on the surface; but he prefers to use the following methods, which he claims as his invention:—Plumbago or black-lead is made to adhere to and enter into the interstices of the fabric, by grinding it very fine, agitating it with water, and immersing the fabric therein; and in some cases the fabric may be boiled in it. A compound of iron and zinc is produced by subjecting a mixture of pieces of iron and zinc, for some hours, to a temperature just below that at which it distils, in an iron vessel, closely luted, with a pipe proceeding therefrom, as is usual in distilling zinc. A crystalline compound is thus produced, which is ground into fine powder, and mixed with the black-lead; and as this compound readily reduces many metallic salts, in consequence of its affinity to oxygen, it is very useful in obtaining a metallic sur-

face. Another method of obtaining a metallic surface on one side of the fabric, consists in attaching plates, or other pieces of metal, closely to the other side. To produce a conducting surface of copper, the fabric is impregnated with a salt of that metal, which is then reduced by the aid of the liquid termed *glycerine*. Any of the substances known as reducing agents may be employed for the reduction of the metal in the fabric; and it may also be reduced by connecting the fabric with a galvanic arrangement, so that the hydrogen generated may pass through it. Another mode of reducing metal, particularly applicable to gold and silver, consists in exposing the fabric, which has been impregnated with a metallic salt, to the action of a current of phosphuretted hydrogen or other gases. The fabric is placed in an air-tight chamber, from which, by the admission of hydrogen or ordinary coal-gas, the air is ejected, and passes off through a bent pipe, which terminates under the surface of the water in a pneumatic cistern; the reduction of the metal is then completed by passing phosphuretted hydrogen through the chamber. This gas is generated from phosphorus and a solution of caustic potash, the surface thereof being covered with a portion of æther, which, becoming volatized on the application of heat, expels the air from the retort, and thereby prevents the combustion of the phosphuretted hydrogen. To produce a more perfect union of the fabric and the metal, the patentee sometimes introduces or weaves thin wires into the fabric at intervals. Phosphorus dissolved in sulphuret of carbon (which may be diluted with turpentine) is also used for reducing metallic salts, with which the fabrics are to be impregnated, after having been dipped in the solution of phosphorus.

With regard to the deposition of metal on fabrics, one method consists in covering a sheet of iron on one side with a porous diaphragm (using any of the materials ordinarily employed in sustaining galvanic batteries, but by preference a mixture of equal quantities of plaster of Paris and Roman cement), and fixing the fabric on the other side by means of wax, or any other substance not soluble in the metallic solution. Two or more sheets, thus arranged, are placed in a vessel containing the solution of metal to be deposited, and are connected together by wires, which proceed from each sheet of iron to the cloth on the next sheet, so as to form a galvanic series. The fabric may, if preferred, be made to surround a plate, or other suitably shaped piece of metal, and be attached thereto by paste, or other suitable material; which paste may be mixed with black-lead, or the compound of zinc and iron, or the finely precipitated metal obtained by the aid of *glycerine*. Another method consists in pasting the fabric upon a plate of amalgamated zinc or other metal, and rubbing the compound of zinc and iron upon its surface; it is then placed in a suitable metallic solution, and attached to the zinc plate of a galvanic battery, whilst another plate or piece of the metal to be deposited is connected to the copper plate of the battery.—Sealed April 11, 1843.

THE CHEMICAL GAZETTE.

No. XLV.—September 1, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Volatile Acids of Butter. By J. U. Lerch.

The results of this investigation, executed under the direction of Prof. Redtenbacher, are as follows:—Butter contains four volatile acids, which stand in very simple relation to each other, viz. *butyric acid* = $C^8 H^8 O^4$ (as adopted by Pelouze and Gelis), *caproic acid* = $C^{12} H^{12} O^4$, *capryllic acid* (new) = $C^{16} H^{16} O^4$, and *capric acid* = $C^{20} H^{20} O^4$. Butter sometimes affords, instead of butyric and caproic acids, a distinct acid, *vaccinic acid*, which appears to be equal to the sum of those two acids minus 1 atom of oxygen, and is very readily decomposed into them. The following is the method adopted by the author in preparing them:—

Fresh butter is completely saponified with potash in a still, the soap decomposed in the vessel with dilute sulphuric acid, the head then luted on, and the aqueous liquid drawn off to within a fourth. Fresh water is then added to it, which is again distilled off, and this operation continued as long as the water which passes over possesses any acid reaction. In this manner the volatile fat acids are carried over just as the essential oils; the action of the atmosphere is moreover entirely excluded. From 4 to 5 pints of a milky liquid are obtained from a pound of butter, on the surface of which float drops of oil and particles of hard or smeary fat. The distilled water is immediately saturated in the receiver with barytic water, and allowed to stand well-closed till the end of the distillation. When the distillation is finished, the still is cleansed and the liquid saturated with barytic water, evaporated in it with the head on to about the twentieth part, and the still hot concentrated ley then reduced to dryness in a retort.

The saline mass obtained in this manner consists of two portions, one easy of solution, the other difficult. The more soluble portion consists, according to circumstances, of butyrate and caproate of barytes, or solely of the barytic salt of vaccinic acid; but in this case there is little or no butyric or caproic acids present. The portion difficult of solution consists of the baryta salts of two distinct acids, which Chevreul described together as caprate of barytes. The more insoluble portion amounts to about the twentieth part of the soluble, and the entire mass to about the tenth part of the sapo-

nified butter. To separate the different salts, the residuary saline mass is boiled with about 5 to 6 parts water; one portion dissolves, the other remains behind. The solution of the easy soluble salts is set aside to crystallize; if, on the first crystallization, the crystals which separate have the appearance of benzoate of lime, and do not effloresce, *i. e.* are caproate of barytes, the butyrate of barytes has still to be sought for in the solution; but if nests of small crystals form, which quickly effloresce, and resemble nests of the native carbonate of lime, it is vaccinate of barytes, and it is then unnecessary to look for butyrate and caproate of barytes.

The circumstances under which butter contains vaccinic acid or butyric and caproic acids are not known. The butter of 1842, and likewise that of the following winter, contained, in several experiments, not a trace of any other easily soluble salt of barytes than the vaccinate; while the butter in the summer of 1843 contained no vaccinic acid, but only the other two.

The soluble saline mass, containing the butyric and caproic acids, is dissolved in water and evaporated to crystallization, in order to separate them. Long silky needles, aggregated in bundles, separate even in the first crystallizations; and if the solution has been sufficiently concentrated, nearly the whole of the caproate salt is deposited. The entire solution solidifies to a paste of minute needles, which are separated by pressure from the mother-ley and purified by recrystallization. The remaining ley is now allowed to crystallize spontaneously, which is best effected by exposure to the sun; at first a little caproate of barytes still separates, the form of the crystal then changes, laminæ of mother-of-pearl lustre make their appearance, and all the subsequent crystallizations are nearly pure butyrate of barytes, which is purified by recrystallization.

The saline mass of difficult solution is dissolved in just so much boiling water as is requisite for complete solution, and is filtered while hot. During the cooling the liquid becomes filled with minute scales, of a fatty lustre, of caprate of barytes, which subside in the form of a crystalline precipitate. The decanted mother-ley is again evaporated one-fourth, when a fresh quantity of caprate of barytes separates. This salt is purified by recrystallization. The mother-ley now contains the capryllate in solution; it is evaporated by exposure to the sun, when the salt separates in minute granules and verrucous masses, which are obtained pure by recrystallization.

This is the best method of separating these salts from each other; an absolute separation is impossible, for there always remain mixed crystals and leys, which in small quantities are not worth while working.

Butyric Acid.—The author examined the barytic salt, the silver salt and the æther compound.

The *barytic salt* sometimes crystallizes in small laminæ of mother-of-pearl lustre and in prisms, sometimes in hard granular crusts. According to the author, it is anhydrous and does not melt at 212° (Pelouze and Gelis assert the contrary). On analysing the salt, it should be well mixed with 3 to 4 times its volume of ignited phos-

phate of copper, previous to being mixed with oxide of copper, in order that the carbonic acid may be completely expelled. The following results were obtained :—

	Prismatic salt.		Granular salt.	Equiv.		Calculated.
Carbon.....	31·10	30·85	31·34	8	= 603·83	31·10
Hydrogen	4·55		4·72	7	87·36	4·47
Oxygen	15·33		15·32	3	300·00	15·38
BaO.....	49·02		48·71	1	956·88	49·05
	100·00		100·00		1951·07	100·00

The *silver salt* is obtained as a caseous precipitate by precipitating nitrate of silver with a concentrated solution of butyrate of barytes. If any reduction takes place, vaccinic acid is present. The salt consists of—

Carbon	24·85	8	= 606·8	24·81
Hydrogen	3·63	7	87·3	3·57
Oxygen	11·96	3	300·0	12·27
AgO	59·56	1	1451·6	59·35
	100·00		2445·8	100·00

Butyric Æther is readily obtained by boiling the barytic salt with alcohol and sulphuric acid; it floats on the surface, from which it is removed, washed with water, dehydrated with chloride of calcium, and rectified. It boils at 230°, and consists of—

Carbon	62·29	12	= 910·25	62·35
Hydrogen	10·46	12	149·75	10·25
Oxygen	27·25	4	400·00	27·40
	100·00		1460·00	100·00

Caproic Acid.—The barytic salt crystallizes in long silky needles, aggregated into bundles; it is anhydrous, and undergoes no change by exposure to the air. It consists of—

Carbon	39·58	38·53	39·23	12	= 910·24	39·50
Hydrogen	5·91	6·27	6·09	11	137·27	5·05
Oxygen	13·04			3	300·00	13·02
BaO	41·47			1	956·88	41·53
	100·00				2304·04	100·00

The silver salt is prepared in the same manner as butyrate of silver, but is far more difficult of solution. It is not crystallizable, and consists of $C^{12} H^{11} O^3 + AgO$.

Caproic Æther is prepared in the same way as the butyrate; it separates more readily, boils at 248°, has a stronger taste and smell, but is not so agreeable. It consists of—

Carbon.....	66·81	66·89	16	= 1213·66	66·93
Hydrogen....	11·16	10·99	16	199·67	11·01
Oxygen.....	22·03	22·12	4	400·00	22·06
				1813·33	

Capryllic Acid.—At the ordinary temperature it forms a smeary mass; below 50° it crystallizes in needles, which are of difficult solution in water, have an acid and acrid taste and a peculiar disagreeable odour. The baryta salt separates from hot solutions in brilliant laminæ, but on spontaneous evaporation in white granules. It is anhydrous, is not affected by exposure to the air, does not fuse at 212°, and is very sparingly soluble in water. It consists of $C^{16} H^{15} O^3 + BaO$.

The almost insoluble silver salt furnished on analysis the following numbers :—

Carbon	38·14		16 =	1213·6	38·49
Hydrogen	5·88	6·22	15	187·2	5·93
Oxygen	9·90		3	300·0	9·51
AgO	46·13		1	1451·6	46·07
				3152·4	

The lead salt, which is very sparingly soluble in water, fuses at 212°, and is represented by the formula $C^{16} H^{15} O^3 + PbO$.

Capric Acid resembles capryllic acid in its properties. The baryta salt crystallizes from hot solutions in minute fatty needles and scales, and on spontaneous evaporation likewise in scales, arranged in dendritic groups; it is very difficult of solution, is anhydrous, and not affected by exposure to the air. It consists of—

Carbon	50·26	50·27	20 =	1517·08	50·38
Hydrogen	7·91	7·83	19	237·11	7·87
Oxygen	10·13		3	300·00	9·97
BaO	31·70		1	956·88	31·78
				3011·07	

Vaccinic Acid.—Vaccinate of barytes separates in nests of crystals, which have already been described; they contain water of crystallization, effloresce very readily in the air, become very similar in appearance to chalk, and diffuse a strong odour of butter, while pure caproate and butyrate of barytes do not effloresce in the least, and have scarcely any odour. Vaccinate of barytes is soluble in water to about the same extent as butyrate of barytes; the saturated solution is thick like oil. When vaccinate of barytes is dissolved in water, and again evaporated in a retort, it crystallizes from the solution unaltered; but if the crystals are exposed for some time to the air, they at last lose nearly all their odour, and when dissolved no longer crystallize on evaporation, but in their stead crops of caproate and butyrate of barytes are obtained. The same happens when a solution is exposed to the air for any length of time or boiled in an open dish. No barytes separates in this change, no acid vapours are given off, and the solution remains perfectly neutral. Vaccinic acid therefore saturates exactly the same amount of barytes as the two acids which have originated from it; the relative quantity of the caproate and butyrate of barytes formed is proportionate to the atomic weights of these two salts. If vaccinate of barytes is decomposed by sulphuric acid, with free access of air, the separated

acid removed by distillation, saturated with barytes, and set aside to crystallize, only a mixture of caproate and butyrate of barytes is obtained. On adding some solution of silver to a solution of vaccinate of barytes, a white caseous precipitate is formed, which is soon reduced and smells strongly of butyric acid.

Vaccinic acid has therefore evidently the same capacity of saturation as caproic and butyric acids together, but probably contains less oxygen. Two analyses of the salt, made however before being acquainted with its instability, afforded 46·36, 46·44 per cent. barytes (atomic weight = 4128, 4124). The formula $C^{20}H^{18}O^5 + 2BaO$ requires 46·11 per cent. barytes (atomic weight = 4156). —*Ann. der Chem. und Pharm.*, xlix. p. 212.

On the Sulphate of the Oxide of Chromium. *By* M. E. Kopp.

On examining the action of deoxidizing bodies upon the sulphates at different degrees of saturation, I had occasion to make some very interesting observations respecting the insoluble sulphate of chrome.

This compound, $3SO^3$, Cr^2O^3, is prepared with the greatest ease on projecting by degrees pulverized bichromate of potash into concentrated sulphuric acid, heated to near its boiling-point. A very lively effervescence ensues, owing to the liberation of oxygen, and a violet insoluble powder, which readily occasions somewhat violent ejections, is immediately deposited. On dilution with water, the precipitate subsides with such facility that it is easily washed by decantation; and the acid liquid, containing the bisulphate of potash, does not retain a trace of a salt of chromium.

The sulphate thus obtained forms a very fine green powder, which on exposure to heat changes its colour, and becomes of a rose colour with a faint violet tint; at the same time it acquires an extreme mobility. On cooling, the primitive colour reappears; in this state the salt is altogether insoluble in water, even after long contact. The water employed for edulcoration produces no turbidness in a solution of chloride of barium; it may therefore be employed with advantage in separating oxide of chromium from a number of other oxides. Let us imagine, for instance, a solution containing salts of iron, zinc, alumina, uranium, chromium, &c., it is only requisite to add an excess of sulphuric acid, and to concentrate the liquid by ebullition, in order to separate completely the whole of the chromium in the state of insoluble sulphate, which remains in this state even on adding water, while the other sulphates are held in solution. Nitre oxidizes the sulphate of chromium with extreme facility. This salt, submitted to the action of dry hydrogen at a temperature near to red heat, undergoes a remarkable decomposition. Considering the great stability of the oxide of chrome, we should expect to see products from the reduction of the sulphuric acid by hydrogen disengaged, such as water, sulphurous acid, and secondarily sulphur and sulphuretted hydrogen, while oxide of chromium would be left as residue. Instead of this, however, the whole of the oxygen of $3SO^3$, Cr^2O^3 disappears, either in the state of

water or in the state of sulphurous acid gas; and the reduction is effected with such great energy, that a more intense phænomenon of ignition occurs than that which is observed in the reduction of copper by hydrogen. A portion of the sulphur is given off in the state of SO^2, another in the state of free sulphur. There then remains in the tube a brownish-black pulverulent body, which has so great an affinity for oxygen that it constitutes one of the most energetic pyrophors; in fact, even after having preserved it for weeks in sealed tubes filled with hydrogen, it is impossible to expose the least particle to the air without its igniting and burning with great brilliancy. The products of the combustion are sulphurous acid and oxide of chromium.

This compound is moreover remarkable from its composition. It contains only chromium and sulphur, as was proved by analysis, in which the chromium was determined separately in the state of oxide and the sulphur in the state of sulphate of barytes. It contains but half the sulphur contained in the sulphuret of chromium, $C^2 S^3$, so that its composition should be expressed by $Cr^4 S^3$.

A very simple experiment confirms this composition. On bringing into equilibrium on the balance a sealed tube containing this compound, and then breaking the extremities so that the $Cr^4 S^3$ might fall out, and so become ignited, it is found after oxidation that the equilibrium has not been perceptibly disturbed. In fact, $Cr^4 S^3$ becomes converted by oxidation into $Cr^4 O^6$, disengaging $3SO^2$; but the S^3 lost weight nearly as much as the O^6 gained.

However, the quantity of sulphur is frequently found to be less than that which corresponds to the formula $Cr^4 S^3$, and it appears probable that we may obtain the compound $Cr^2 S$ at a higher temperature; for in those experiments in which the heat was carried to the fusion of the glass, the most considerable losses in weight, from the removal of the oxygen and sulphur by the hydrogen, were observed. It was also remarked in these cases, that the fused glass became coloured so intensely red as to appear nearly opake. From this it would seem, that while the compounds analogous to the oxide of chrome possess the property of colouring glass green, the compounds of inferior degree impart to it a red colour. In this respect there is some analogy between the compounds of copper and those of chrome.

I. 6·265 grms. sulphate of chrome treated with hydrogen lost 3·76 grms.

If the residuary compound had been $Cr^2 S^2$ it should have lost 3·51
... ... $Cr^2 S$ ... ... 4·00 } $\frac{7·51}{2} = 3·75$.

The result observed is the mean $Cr^2 S^2 + Cr^2 S = Cr^4 S^3$.

II. 5 grms. of $3SO^3$, $Cr^2 O^3$ lost 3·01 grms.

$Cr^2 S^2$ would require 2·802.
$Cr^2 S$ would require 3·201.

The result observed is again the mean. But in the experiment in which the greatest loss occurred it amounted to 3·11 in 5 grms., which brings it near to the composition of $Cr^2 S$.

Supposing this oxidized compound to correspond to $Cr^4 S^3$, we should have the following series of oxides of chrome, $Cr^4 O^3$, $Cr^2 O^3$, CrO^3, in which the quantities of metal are in the proportion of 4 : 2 : 1.

The compound $Cr^4 S^3$, in contact with aqueous vapour, is decomposed when hot with disengagement of hydrogen and sulphuretted hydrogen, and becomes converted into oxide of chrome; it is therefore requisite to dry the hydrogen very carefully so as to avoid a mixture of the oxide of chrome with the sulphuretted compound. In contact with dry chlorine $Cr^4 S^3$ burns very energetically, and is converted into perfectly pure $Cr^2 Cl^6$ of a beautiful rose colour, while the sulphur forms a subchloride of sulphur. The chloride of chromium, $Cr^2 Cl^6$, submitted to the action of hydrogen, loses a large quantity of chlorine, which is liberated in the state of hydrochloric acid gas, and the loss in weight seems to indicate the formation of the compound $Cr^4 Cl^6$.—*Comptes Rendus*, June 17, 1844.

Further Researches on Iodine. *By* M. Millon.

Action of Nitric Acid on Iodine.—The various hydrates of nitric acid differ in their action on iodine as much as on the metals. The presence of nitrous acid equally modifies the reaction in the most remarkable manner. Thus nitric acid with $4\frac{1}{2}$ equivalents of water does not oxidize iodine, but merely dissolves it with the assistance of heat; nitric acid with 3 equivalents of water converts it into iodic acid; nitric acid with 1 or 2 equivalents of water converts the iodine into a new oxide, inferior to all those hitherto discovered, and leads to the production of a peculiar acid, which is represented by the formula IO^4, hypo-iodic acid.

The influence of nitrous acid is felt on the three hydrates above mentioned, but it is especially with respect to the iodic acid that this difference is manifested; for while nitric acid with $4\frac{1}{2}$ equivalents of water readily dissolves iodic acid, the same acid mixed with a small quantity of nitrous acid reduces the iodic acid, and gives rise to a deposit of iodine.

Action of Sulphuric Acid on Iodic Acid.—M. Gay-Lussac, in giving the general history of iodine, has confined himself to stating that sulphuric acid decomposes iodic acid into iodine and oxygen. Davy, investigating the same subject, pointed out a yellow compound, which he considered to be a combination of the two acids. Serullas endeavoured in vain to reproduce the combination described by Davy, and considered himself justified in denying its existence.

In examining this reaction, apparently so simple, but nevertheless controverted by eminent chemists, I have discovered the production of a dozen new, solid, crystalline compounds, of a perfectly definite but somewhat peculiar constitution. The following are the phænomena which occur in the action of sulphuric on iodic acid, and which may readily be observed in a small glass flask with the assistance of a spirit-lamp.

At a temperature near to its boiling-point, the sulphuric acid dissolves the iodic acid in the proportion of a fifth by weight. If,

after the iodic acid has dissolved, heat be still applied, an evolution of pure oxygen takes place without any mixture of iodine. From the moment oxygen is liberated, the liquid becomes coloured deeply yellow, which tint augments with the production of gas. Subsequently, on continuing the application of heat, the sulphuric acid becomes greenish; iodine then appears, and accompanies the liberation of the oxygen to the end. On arresting the reaction at different periods, which are very distinct, there is obtained from the sulphuric acid—

1. Several combinations of sulphuric and iodic acids.
2. Compounds formed by the union of the three acids, iodic, hypo-iodic and sulphuric.
3. Combinations of hypo-iodic and sulphuric acids.
4. Some combinations of sulphuric acid and of a peculiar acid of iodine, containing still less oxygen than hypo-iodic acid, agreeing with the formula $I^5 O^{19}$, and which may be called sub-hypo-iodic acid.

All these compounds exist only under peculiar conditions, otherwise they are destroyed with great rapidity; for instance, they are only permanent in perfectly dry air or in concentrated sulphuric acid. These circumstances render their examination very difficult, and from all of them being formed solely by the contact of boiling sulphuric and iodic acids, it will be understood what care must be taken to arrest the action in time, and to separate these different products one from the other. Nevertheless a dozen different compounds have been isolated and analysed with exactitude; a far greater number is certainly produced. I should however add, that from the mode of separation employed, only the insoluble and crystallizable products have been analysed. If some soluble combinations of sulphuric acid with IO^5, IO^4, $I^5 O^{19}$ exist, or even with other oxygenized combinations of iodine, they must have escaped my observation; but the products described will, I hope, suffice to establish the view which I have adopted.

It suffices to look at the formulæ representing these compounds to be struck with their novelty. Next, to what order of compounds should these peculiar combinations be arranged? How should their constitution be represented? What idea should be entertained with respect to their production? These questions result from the investigation of these different products, for they are exceedingly interesting in a theoretical point of view.

These compounds, represented in their formulæ by the association of two or three acids, do not at present appear susceptible of any other interpretation. They are complex products, resulting from several acids combined together, placed with respect to each other in as evident an antagonism, or in as complete an electrical opposition, as if it were question of an alkaline oxide in the presence of a strong acid.

This certain and varied union of several acid principles indicates precisely the character of novelty of the products.

Some doubts have been entertained respecting the actual combina-

tion of mineral acids with one another. The combination of chromic and sulphuric acids, pointed out by Gay-Lussac, is in fact contested or denied by some experienced chemists. The products which result from the union of sulphuric acid with the nitric and nitrous compounds have scarcely been indicated. One of them has been analysed to favour a peculiar systematic view; but such compounds as IO^5, HO + $3SO^3$, HO; $2IO^5$ + IO^4 + SO^3, HO; IO^4 + $2SO^3$, HO, &c., leave no room for doubt.

As a very general consequence of the study of the compounds which result from the action of the sulphuric acid on iodic acid, it may be concluded that acids have no less a tendency to combine with each other than with bases, and perhaps than bases with each other. This tendency is especially manifest in some peculiar circumstances of atmosphere and of medium; but it prevails even in the midst of a solvent which may be considered as opposed to such combinations.

The explanation of certain compounds, such as the emetics and alums, which hitherto have presented a kind of anomalous constitution, will be found in this tendency. Assigning constantly to alumina, to peroxide of iron, and those oxides of the same formula, $M^2 O^3$, the part of an acid, and arranging the combinations they form with acids by the side of the compounds produced by sulphuric and iodic or hypo-iodic acids, their nature will be rendered more generally intelligible.

Investigation of two new Oxygenized Compounds of Iodine.—The discovery of these two new combinations, which are produced by the action of nitric acid on iodine and of sulphuric on iodic acid, furnishes new points of affinity between the series of chlorine and that of iodine.

These two acids, which are represented, the one by IO^4, the other by $I^5 O^{19}$, will be placed by the side of hypochloric acid, ClO^4, and of the acids, chloro-chloric, $Cl^3 O^{13}$, and chloro-perchloric acid, $Cl^3 O^{17}$. The sub-hypo-iodic acid is obtained in several ways; it is purified without difficulty, and the analytical method, by means of which its composition is determined, is susceptible of great accuracy. The polyatomic mineral acids, such as $Cl^3 O^{13}$, $Cl^3 O^{17}$, which I have already had occasion to describe, thus acquire a fresh degree of evidence.—*Comptes Rendus*, June 3, 1844.

Researches on Mannite and on the Decomposition of the Lactate of Lime by Heat. By M. Favre.

The mannite employed in the author's experiments contained 39·24 per cent. carbon and 7·8 hydrogen, and corresponded therefore to the formula $C^6 H^7 O^6$. It melted at 331° Fahr., and solidified again at 324° without losing in weight. It quickly reduced oxide of silver, dissolved without change in potash, barytes and lime when sufficiently dilute, and appeared to combine with lead in several proportions.

Mannitate of Lead.—When an excess of hot ammoniacal solution

of sugar of lead is added to a concentrated solution of mannite, no precipitate is formed; but on cooling, minute asbestos-like laminæ are deposited, which should be collected on a filter, carefully excluding all carbonic acid, and then pressed between blotting-paper, and dried *in vacuo* over sulphuric acid and lime. They are then perfectly white, but become yellow at 266°, without however parting with the whole of their water. They consist of—

Carbon.....	12·19	12·12	6	12·16
Hydrogen.....	1·70	1·67	5	1·69
Oxygen			4	10·81
Oxide of lead	75·00	75·58	2	75·34
				100·00

Exactly the same compound is obtained on precipitating with alcohol a solution of mannite to which an ammoniacal solution of sugar of lead had been added. If this compound be washed on the filter with boiling water, it is converted into a white powder, which, dried with exclusion of carbonic acid, exhibited the following composition:—

Carbon	8·88	8·76	6	8·83
Hydrogen	1·29	1·19	5	1·22
Oxygen			4	7·84
Oxide of lead	81·88	82·45	3	82·11
				100·00

The liquor separated from this powder deposited on cooling a white granular precipitate, which dried at 266° contained 75·29 PbO, 12·25 C, 1·72 H; it is therefore the above described bibasic salt. After the separation of this salt, the solution afforded on evaporation a residue, which contained only 67·9 per cent. oxide of lead; it is therefore probably a mixture of the bibasic compound with PbO, $C^6 H^5 O^4$. It is consequently certain that mannite, on combining with oxide of lead, parts with 2 equiv. water.

Mannite and Sulphuric Acid.—On pouring concentrated sulphuric acid over mannite, it dissolves to a colourless solution, but with evolution of heat; it is diluted with water, neutralized with chalk, the liquid decomposed with acetate of barytes, and the sulphate of barytes removed by filtration. The solution obtained is rendered turbid on boiling by the separation of some sulphate of lime; alcohol precipitates mannito-sulphate of lime; neutral acetate of lead affords a slight, basic acetate, an abundant precipitate. On collecting the latter on the filter, washing it with boiled distilled water, pressing it between blotting-paper, and drying it *in vacuo*, it formed a white powder, insoluble in water, soluble in acidulated water without effervescence and without liberation of acetic acid, and which, dried at 266°, gives—

Carbon.....	5·98	6·09	6	6·01
Hydrogen	0·85	0·79	5	0·83
Oxygen			4	
Sulphuric acid....	13·30	12·90	2	13·37
Oxide of lead	88·17	87·85	4	87·82

The compound is decomposed with difficulty by boiling water, and even when it is dissolved in nitric acid it is a considerable length of time before it deposits sulphate of lead.

If the lead compound is decomposed by sulphuretted hydrogen, and the filtered liquid concentrated *in vacuo*, the mannito-sulphuric acid is obtained in solution; it does not precipitate salts of barytes and lime in the cold, but only when boiled.

Action of Caustic Lime upon Mannite.—When mannite is distilled with 8 times its weight of caustic lime, the same phænomena occur as in the distillation of sugar with lime, hydrogen is disengaged, and water and a light oil pass over into the receiver; the water contains no acetone. The oil behaves like metacetone; it dissolves in alcohol and æther, has an æthereal smell, dissolves without alteration in hydrochloric acid, and is blackened by sulphuric acid.

Distillation of the Lactate of Lime.—When lactate of lime is heated in a retort, it first parts with much water, melts, again solidifies, and then disengages carbonic acid, while water and the oil, resembling metacetone, pass over into the receiver. The water likewise contains no acetone. It is necessary to apply a pretty strong heat to render the decomposition complete throughout the whole mass; on this account the products are more coloured than with mannite. The oily product does not exhibit a perfectly constant composition; that which distils over at 183° has the composition of metacetone; that between 320° and 356° contains an excess of carbon and hydrogen in the proportion of C H.

Carbon	73·22	74·62	77·42
Hydrogen	10·17	10·40	10·84

The author could not succeed in purifying the oily product completely; when, however, it is distilled quickly over an Argand lamp, the distillate contains much acetone. The portion which distils over without boiling between 320° and 356° constantly exhibits the composition given in the third analysis.

The decomposition of lactic acid appears therefore to be as follows:—$4(C^6 H^6 O^6) = 6CO^2 + 9HO + 3(C^6 H^5 O)$.—*Ann. de Chim. et de Phys.*, t. xi. p. 71–81.

ANALYTICAL CHEMISTRY.

On the Blue Colour produced in Tincture of Guaiacum by various Reagents. *By* H. Schacht and W. Müller.

The production of the above colour on mixing tincture of guaiacum with *Vinum Sem. Colchic.* has given rise to two independent treatises on the subject, of which the following is a short abstract.

M. Schacht made the following experiments:—

1. Freshly prepared *chlorine water*, free from muriatic acid, when mixed with the tincture diluted with alcohol, immediately produced a beautiful blue colour, which was soon transformed into green, and

in a few minutes entirely disappeared. The solution was rendered strongly acid, had lost its odour of chlorine, did not bleach litmus-paper, and produced no vapours of muriate of ammonia when pure ammonia was brought near it. Upon reapplication of chlorine water, the blue colour was reproduced, but subsequently disappeared, and on the addition of water brownish-green resinous flakes were thrown down.

2. Solution of *chloride of lime* likewise produced in the tincture, diluted with alcohol, a deep blue colour, which soon became green; after the lapse of half an hour, the colourless liquid contained only flakes of a brownish-gray resin.

3. *Nitric acid* produced no alteration, but that containing nitrous acid immediately produced a blue colour, which speedily disappeared.

4. *Nitric oxide*, developed from nitric acid and copper, and introduced into the diluted tincture, after admixture with air, produced a blue colour; but this disappeared in a few minutes. When a bottle, into which the tincture had been put immediately after the addition of the gas, was opened, the colour reappeared.

5. A few drops of the *Tinct. guaiaci*, mixed with acid *Spirit. æther. nit.*, produced a blue colour immediately; after five minutes the liquid was colourless.

6. *Spirit. æther. nit.*, rendered neutral by calcined magnesia, when first mixed with a few drops of the tincture, remained transparent, but in a few minutes had a bluish tinge, and subsequently became gradually deeper until it was dark blue; it remained so for two hours, but after eighteen hours it had become bright brown. In a bottle which was completely filled and stoppered, and in which a strip of litmus-paper was put, the same appearance was produced; at the end of twenty-four hours the blue colour had disappeared, and the litmus-paper was slightly reddened.

When the tincture mixed with the *Spirit. æther. nit.*, and magnesia added, was agitated in a stoppered bottle, it did not become so quickly coloured, but just as strongly, and retained this colour for nearly twenty-four hours; but when a few drops of nitric or sulphuric acid were added to the acid *Spirit. æther. nit.*, the blue colour immediately appeared, but disappeared as quickly. Is the nitrite of the oxide of ethule, in this instance, more readily decomposed by the action of the stronger free acid, and the nitrous acid, which alone can produce the colour, set free, and which decomposition first gradually ensues in the neutral *Spirit. æther. nit.*? or should we not rather be right in considering that in the acid *Spirit. æther. nit.* free nitrous acid is always present? To prove that the *Spirit. æther. nit.*, which had become acid, contained free nitrous acid, the behaviour of the nitrite of potash might serve; for the aqueous solution of the latter did not colour the *Tinct. guaiaci*, but after a time merely produced a greenish tinge; whilst another portion of the solution of nitrite of potash, heated with a drop of diluted sulphuric acid, was immediately coloured strongly blue on the addition of the tincture.

7. *Solution of perchloride of iron*, perfectly free from chlorine,

diluted with water, mixed with a few drops of the tincture, immediately produced a blue colour.

8. *Pernitrate of mercury* (perfectly free from the protonitrate), added to the tincture, diluted with distilled water, immediately produced a bright brown colour, and a voluminous, caseous, bluish-white precipitate separated. The clear filtered liquid gave with pure ammonia a grayish-black, with chloride of sodium a white precipitate. It is thus evident that the guaiacum resin has a great tendency to become oxidized, and the blue colour is an intermediate oxidized compound, which is converted into a dark brown resin, more *slowly* or *rapidly* according to the oxidizing influence of the matters present, or exposure to atmospheric air.

9. Taddei has shown that gluten is coloured blue by *Tinct. guaiaci.* The author tried the following substances:—

a. Oats, pounded with cold distilled water, yielded a filtered liquor, which was immediately coloured blue by *Tinct. guaiaci.*

b. Barley exhibited the same appearances.

c. Solution of rye, prepared in a similar manner to oats, yielded a similar colour.

d. Colchicum seeds, the same.

e. Also pæony seeds.

f. *Datura stramonium*, the same. As also

g. *Althæa officinalis.*

h. The expressed and filtered juice of the common onion behaved in the same manner as the barley.

i. Gum-arabic, freshly dissolved in water, and mixed with tincture of guaiacum, yielded likewise a blue colour.

k. Tragacanth, similarly treated, yielded a milky solution, which after six hours had a greenish tinge.

l. Jalap, treated with either hot or cold water, yielded no colour, nor did the mucilage from quince or flax-seed.

m. Arrow-root, treated with cold water, gave with the tincture at first a milky-white solution, which gradually became blue. When treated with boiling water no colour was produced.

n. Cow's milk was immediately coloured blue by the tincture, but in half an hour became white. When boiled no colour was produced.

o. Caseine of milk, separated without the use of acid, and dissolved in water by means of a little *sodæ carb.*, produced no colour; nor did the whey separated without acid.

p. Neither egg-albumen, isinglass, cane or milk-sugar, when agitated with water, yielded any colour.

q. The bruised grains of oats, barley, rye and colchicum, when treated with absolute alcohol, gave a solution which yielded no colour with the tincture; but when diluted alcohol was used, the solutions were strongly coloured blue.

r. Slices of potatoes, onions, and several other roots, especially the roots of the *Hydrocharis morsus ranæ*, when moistened with the tincture, became immediately blue. Since the substance producing the blue colour occurs abundantly in the latter root, a quantity of

it was submitted to pressure, and the juice strained through a cloth to separate it from starch. This liquid coloured the tincture of a beautiful indigo-blue, while the boiled juice produced *no* change. Some of the expressed juice, to which alcohol was added, deposited white flakes of albumen, and coloured the tincture of a beautiful dark blue, not however immediately after filtration. Some of the same juice with alcohol no longer produced any colour after boiling.

The juice of the root of *Hydrocharis*, freed as above directed from albumen, left on evaporation at 122° to 140°, in a porcelain dish, a yellowish viscid mass, soluble in water but *not* in absolute alcohol. A few drops of the tincture added to the aqueous solution gradually coloured it pale blue, and after some time it deposited a blue resin; alcohol added to the tincture produced no colouring. The extract, purified with alcohol and evaporated spontaneously, left the same viscid yellow mass, which, dissolved in weak spirits, was instantly coloured of a deep blue by guaiacum tincture. The colouring substance therefore must be partially changed even at 140°, since the spontaneously evaporated extract acquired a far deeper colour.

The behaviour of *Vinum sem. colchici*, which, like the aqueous extract, colours the tincture strongly blue, is remarkable, for when boiled it no longer produces any colour. In this case, therefore, the gluten must have been altered on boiling by one of the constituents of the wine, probably the alcohol, since, as related under *Hydrocharis*, the juice, treated with alcohol, produced no colour after boiling. 2 drms. of *Sem. colchic.*, prepared in the cold, were boiled with 1 drop of alcohol, for the purpose of deciding this question; and, in fact, the tincture *was no longer rendered blue*. Aqueous extracts of barley, oats, wheat and *Althea*, boiled with 1 drop of alcohol, presented exactly the same appearances. It is evident therefore that the gluten is modified on boiling even by the smallest quantity of alcohol. Starch and albumen appear to produce a similar change in this substance. The cold extract of *Althea*, boiled with a trace of albumen from a hen's egg, produced on cooling no colour with the tincture, which otherwise, as above stated, was the case. It may be, therefore, that on heating the juice of the *Hydrocharis*, the vegetable albumen still contained in it may have produced the change. This likewise explains the behaviour of milk, the caseine of which is modified on boiling by the albumen, which is present in larger or smaller quantity in all animal fluids.

M. Schacht does not venture to decide whether gum-arabic contains gluten, or whether the colouring property is peculiar to it; nor are the colouring substances altered in this case by boiling*.

Müller confirms by experiment the statements of Schacht relative to the action of the soluble proteine compounds. Müller found that, of all the preparations of colchicum, only the *Vinum sem. colch.* and the infusion (not however the decoction) colour tincture of guaiacum blue. Solution of sugar, quince, mucilage and the decoc-

* It appears therefore as if the production of the blue colour in guaiacum tincture was peculiar to several proteine compounds in their soluble modifications.

tion of *Althea*, did not colour the tincture blue; gum-mucilage gradually produced a blue colouring. If the aqueous or spirituous extract of the colchicum-seed is precipitated with absolute alcohol, a white flocculent sediment is obtained, which itself does not colour the tincture, but its aqueous solution immediately turns it blue. Neutral acetate of lead produces in both of the extracts a yellowish-white precipitate; the filtered liquid turns guaiacum tincture blue, while the liquid filtered from the precipitate with *basic* acetate of lead has no such effect.

The expressed juice of some young plants of barley coloured the tincture immediately blue. Vegetable caseine dissolved in alcohol, and gluten suspended in water (in both therefore the insoluble modification), produced no change, nor did emulsine and animal (coagulated?) albumen. Whether therefore guaiacum tincture can be employed, as proposed by the author, for the purpose of distinguishing vegetable from animal albumen, must still remain uncertain; since it has not been shown whether vegetable albumen does not produce the blue colour likewise in its coagulated state, and animal albumen also in its soluble form.—*Archiv der Pharm.*, xxxv p. 3–15 and 262–264.

CHEMICAL PREPARATIONS.

Formulæ for some Trochisci. *By* M. Schmitz.

Trochisci Althææ.—℞ *Rad. Alth. Pulv.*, ʒij.; *Rad. Glycyrrhiz.*, ʒss.; *Rad. Iridis*, ʒj.; *Sacch. Albi.*, lbij.; *Mucil. Tragac.*, q. s.

Trochisci Bechici (according to Vignier):—℞ *Succ. Glycyrrh. Pulv.*, ʒxx.; *P. Gum. Acaciæ*, ʒv.; *P. Sacch. Alb.*, ʒxx.; *Opii pulver. gr.* lxxxiv.

Mix with about 10 oz. of water to form a mass, from 6 drms. of which thirty lozenges are to be made.

Trochisci Catechu.—℞ *P. Catechu*, ʒvij.; *Rad. Iridis*, ℈ij.; *P. Sacch. Alb.*, ʒiij.; *Ol. Rosar.*, ♏iv.: *Mucil. Tragac.*, q. s.

Either 2-grain pills or small lozenges are to be made from this, and sprinkled with powdered violet-root. The oil of roses may be replaced by oil of cloves, cinnamon or peppermint.

Trochisci Gummi.—℞ *P. Acaciæ Gum. Sacch. Albi*, āā., ʒiv.; *Aq. Rosæ*, ʒix.

The latter may be replaced by 4 drops of oil of roses and water, or by orange-flower water. It is best not to mix up more of this than the quantity stated, because the gum very quickly becomes dry.

Trochisci Ipecacuanhæ.—℞ *P. Rad. Ipec.*, ʒx.; *Sacch. Alb.*, ʒxxiv.; *P. Catechu*, ʒss.; *Mucil. Tragac.*, q. s.

An ounce of these lozenges contains 30 grs. of Ipecacuanha, and each one weighing 5 grs. $\frac{1}{4}$ gr. of the root.

Trochisci Rhei.—℞ *P. Rhei*, ʒss.; *Sacch. Alb.*, ʒvss.; *Ol. Menth. Pip.*, ♏xij.; *Aq. Menthæ Pip.*, q. s.

Trochisci Strumales.—℞ *Sacch. gross. pulv.*, ʒxxx.; *Aq. Rosæ*, ʒiv.; *ad consist. Trochiscor. coque, et ab igne remove, dein adde pulv. sequent.*, ʒiij. + ʒvj.:—

℞ *Spongiæ ustæ*, ʒiv.; *Oss. Sepiæ, Lapid. Spongiæ āā*, ʒij.; *Nuc. Gallar., Cinnam. ft.*, ʒj.; *M. P. Pulv. subtiliss. Fiant Trochisci secund. artem.*

Trochisci de Vichy.—℞ *P. Sodæ Bicarb.*, ℈xvj.; *Sacch. Albiss.*, ʒxvj.; *Mucil. e Tragac. pulv.*, ʒss.; *Aq. Comm.*, ʒxj. *ut ft. Trochisci.*

The most various recipes exist for these lozenges. The above is said to have been deduced from the analysis of true *Tablettes de Vichy*. They are rendered aromatic by the addition of balsam of Tolu, oil of peppermint (gtt. vi.), and mixing with orange-flower water.

Trochisci effervescentes.—

Troch. Acidi.	Troch. Alkalini.
℞ *P. Acid. Citric.*, ʒiv.	℞ *P. Sodæ Bicarb.*, ʒiv.
Sacch. Albi, ʒviij.	*Sacch. Albi*, ʒviij.
Ol. Citr., ♏xij.	*Muc. Trag.*, q. s.
Mucil. Trag., q. s.	

The acid lozenges become moist, and must therefore be preserved in stoppered bottles.

Trochisci Cinchonæ.—℞ *Extr. Cinch. flav.*, ℈iv.; *P. Cort. Cinch.*, ℈viij.; *P. Sacch. Alb.*, lbj.; *Aq. font.*, ʒvj.—*Archiv der Pharm.*, xxvii. p. 329.

Precipitation of Morphia from Tincture of Opium by Ammonia.

As is well known, tincture of opium and *Liq. Ammoniæ anisatus* are frequently prescribed in combination. M. Reinsch observed, that such a mixture, after standing for twenty-four hours, deposited morphia in the crystalline form; this may be prevented by the addition of alcohol.—*Jahrb. für Prakt. Chem.*, viii. p. 29.

[The carbonate, or the aromatic spirit of ammonia, which are more frequently ordered in this country, produce the same decomposition. —Ed. *Chem. Gaz.*]

Extractum Taraxaci.

Dr. Bley, who has made some comparative experiments on this extract, states that he obtained, in the spring, from 32 lbs. of fresh root with the green parts, by pressure 10 oz., by infusion 18 oz., by decoction 19 oz. of extract; in autumn, from fresh roots with the green parts, by infusion 37 oz.; and from 13½ lbs. of dry roots (equal to 40 lbs. of fresh), by infusion 38 oz. of extract. The extracts prepared in the spring were all brown, of the peculiar odour and bitter saline taste; the extracts prepared in the autumn were, on the contrary, yellowish-brown, and possessed a sweetish odour and

taste. On solution in water, the extracts prepared in spring deposited much less inuline than those made in autumn. The extract obtained by pressure is most active, but is also the dearest; the infusion, over which the decoction has no advantage, is preferred. Perhaps it would be best first to express the plant, then to infuse the residue in a little hot water for a few hours, to express again and to proceed as usual.—*Archiv der Pharm.*

Decomposition of the Golden Sulphuret of Antimony by Light.

M. Ingenohl has observed, that carefully prepared golden sulphuret, which has been quickly dried in a shady place, keeps for a long time in dark vessels undecomposed, but becomes paler when exposed to light, and then yields on analysis an amount of oxide of antimony and sulphuric acid. Wackenroder confirms this observation, and likewise that of Otto, that the precipitated golden sulphuret always contains an amount of oxide when dried by exposure to the air. The preparation precipitated from the sulphuret of antimony and sodium does not undergo so remarkable a decomposition by light.—*Archiv der Pharm.*, xxxv. p. 255.

Heusler's Charta Vesicatoria.

Yellow wax, ℥iss; oil of cantharides, ℥j; spermaceti, ʒvj; larch turpentine, ʒij, are melted together, and the mass when nearly cold is spread upon paper with a spatula. The following plaster, likewise spread on paper, is recommended for confining it to the intended place:—Lead plaster, ℥vj; purified rosin, yellow wax, olive oil, of each ʒij; turpentine, ʒv. Mix.—*Jahrb. für Prakt. Pharm.*, p. 369.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Source and Nature of Colouring Substances of Organic Origin, and on the Action of Oxygen upon them. By F. Preisser.

[Continued from page 372.]

Barwood or Camwood.

Some account of a wood very much employed in England, known under the names of Barwood and Camwood, and which possesses great analogy with saunders-wood, will not be without interest. The following is extracted from an article drawn up by M. Girardin and myself some years ago, but which has not been published:—

Afzelius discovered, in the colony of Sierra Leone, a lofty and fine tree, bearing white flowers, belonging to the *Leguminosæ*, to which he gave the name of *Baphia nitida*. DeCandolle placed this genus, with some doubt, near *Pterocarpus*, which furnishes the saun-

ders-wood. A drawing of this is given in Loddiges' 'Botanical Cabinet*.' The Portuguese imported the wood into Europe sixty years ago†. It is in England only that it has been used. The dark red which is commonly seen on the English bandana handkerchiefs, is generally produced by the colouring matter of the barwood, rendered darker by sulphate of iron. According to MacCulloch, the importation of this wood rose in 1829 to 246 casks 15 cwt. In 1833, in the London market, it was worth from 9*l.* to 11*l.* the cask, a duty of 5*s.* included‡. MacCulloch makes a distinction between barwood and camwood; but it is the same wood, only coming from two different places on the coast of Africa§.

The wood which M. Girardin and I experimented upon came from England.

This wood, in the state of a coarse powder, is of a bright red colour, similar to that of saunders-wood, without any odour or smell. It imparts scarcely any colour to the saliva.

Cold water, in contact with this powder, only acquires a fawn tint after five days' maceration; 100 parts of water only dissolve 2·21 of substances consisting of 0·85 colouring matter and of 1·36 saline compounds. Boiling water becomes more strongly coloured of a reddish yellow, but on cooling it deposits a part of the colouring principle in the form of a red powder. 100 parts of water at 212° dissolve 8·86 of substances consisting of 7·24 colouring principle and 1·62 salts, especially sulphates and chlorides. On macerating the powder in strong alcohol, the liquid almost immediately acquires a very dark vinous red colour. To remove the whole of the colour from 1 grm. of this powder, it was necessary to treat it several times with boiling alcohol. The alcoholic liquid contained 0·23 of colouring principle and 0·004 salt; barwood contains therefore 23 per cent. of red colouring matter, whilst saunders-wood, according to Pelletier, only contains 16·75.

The alcoholic solution behaves in the following manner towards reagents:—

Distilled water, added in great quantity	Produces a considerable yellow opalescence. The precipitate is redissolved by the fixed alkalies, and the liquor acquires a dark vinous colour.
Fixed alkalies	Turn it dark crimson or dark violet.
Lime water	Ditto.
Sulphuric acid	Darkens the colour to a cochineal red.
Sulphuretted hydrogen	Acts like water.
Salt of tin	Blood-red precipitate.
Chloride of tin	Brick-red precipitate.
Acetate of lead	Dark violet gelatinous precipitate.
Salts of the protoxide of iron	A very abundant violet precipitate.
Copper salts	Violet-brown gelatinous precipitate.

* Vol. iv. fig. 367.

† Bancroft, Philosophy of permanent Colours. Dampier, vol. ii. part 2, p. 58.

‡ MacCulloch, A Dictionary, Practical, Theoretical and Historical, of Commerce and Commercial Navigation, 1835, p. 123.

§ Ibid, p. 216.

Chloride of mercury	An abundant precipitate of a brick-red colour.
Nitrate of bismuth	Gives a light and brilliant crimson red.
Sulphate of zinc	Bright red flocculent precipitate.
Tartar-emetic	Abundant precipitate of a dark cherry colour.
Neutral salts of potash	Act like pure water.
Water of barytes	Dark violet-brown precipitate.
Gelatine	Brownish-yellow ochreous precipitate.
Chlorine	Brings back the liquor to a light yellow, with a slight yellowish-brown precipitate, resembling hydrated peroxide of iron.

Pyroxylic spirit acts on barwood like alcohol, and the strongly coloured solution behaves similarly towards reagents. Hydrated æther almost immediately acquires an orange-red tint, rather paler than that with alcohol. It dissolves 19·47 per cent. colouring principle. Ammonia, potash and soda, in contact with powdered barwood, assume an extremely dark violet-red colour. These solutions, neutralized with hydrochloric acid, deposit the colouring matter in the form of a dark reddish-brown powder. Acetic acid becomes of a dark red colour, as with saunders-wood.

The colouring matter was extracted from the barwood in the same manner as from saunders-wood. It presented the same characters, and we therefore consider it to be identical with the latter.

The red colour obtained from barwood is brilliant, but it is not so permanent as that from madder. Soap turns it brownish, but the brown is perfectly fast. A great variety of shades are produced by the use of quercitron, and other tinctorial madders, with the barwood; but in these cases the colouring matters are applied one after the other.

Camwood affords analogous colours; but it is not used, its price being nearly twice as much as that of barwood, and the tints it produces are less permanent.

[To be continued.]

On the Bleaching of yellow Bees-Wax. By M. Ingenohl.

A very expeditious method of bleaching wax is by the application of nitric acid in the following manner:—A pound of yellow bees-wax is melted, and freed by straining from impurities; 2 oz. of nitrate of soda are then added to it, and subsequently by degrees 1 oz. of sulphuric acid, which has been previously diluted with at least 9 parts of distilled water; the whole mass is kept warm, and constantly stirred with a glass rod. The vessel must be spacious, especially very high, as the mass rises considerably. When the whole of the dilute sulphuric acid has been added, it is allowed to cool somewhat, the vessel filled with boiling water, well-agitated and set aside. The wax-cake is removed, and conveyed into boiling water until this no longer removes any sulphate of soda from it, and consequently does not produce any turbidness in a solution of

chloride of barium; the wax is then perfectly white. By the melting in water every trace of nitric acid is removed, which, were it present, would be decomposed on exposure to light into oxygen and nitrous acid, and would thus impart a reddish colour to the wax.—*Archiv der Pharm.*, xxvii. p. 285.

On the Fixation of Photographic Images by means of a Silver Bath.

Plunge the plate into a silver-bath (cyanide of silver dissolved in cyanide of potassium) upon removing it from the mercury, let it stand for a few seconds until the sensitive coat is dissolved, then establish the galvanic current. In eight or ten seconds the proof is fixed.

Its advantages are,—1st, it gives such great brilliancy to the lights, that the solarized parts become generally beautifully white; 2nd, silver being a photogenic metal, the plates may be easily reprepared for use by rubbing with dry tripoli; 3rd, if you pour over a proof, when taken from the mercury, or when fixed by silver or chloride of gold, concentrated hyposulphite, and bring the liquid nearly to boiling, the proof gradually takes the most rich tints, passing successively from yellow to red, and from red to blue; the zinc pole determines these colours in the cold at the points near it. Proofs already fixed by chloride of gold give the richest colours.—*Journ. Frankl. Instit.* for May 1844.

PATENT.

Patent granted to Joseph Bower, Hunslet, York, *for certain Improvements in the Manufacture of Carbonate of Soda.*

This invention consists in using the bicarbonate or sesquicarbonate of ammonia to decompose sulphate of soda, for the purpose of producing carbonate of soda.

The mode of operating is as follows:—Into an iron cylinder, containing an agitator, 200 parts of water, 86 of bicarbonate of ammonia, and 100 of anhydrous sulphate of soda, are put, and agitated for a period varying from eighteen to thirty-six hours. From the reaction which takes place, bicarbonate of soda and sulphate of ammonia are produced; the bicarbonate of soda is then drained and filtered; and, in order to separate from it all the solution of sulphate of ammonia, the mass is also submitted to pressure. The bicarbonate of soda may now be converted into the ordinary carbonate of soda, by subjecting it to a low red heat in a retort or close furnace, in connexion with a cooled receiver, by which means any ammonia that may remain will be collected.

When the sesquicarbonate of ammonia is used, a current of carbonic acid gas is introduced into the cylinder, while the mixture is being agitated, to convert the free ammonia present into bicarbonate of ammonia.—Sealed March 4, 1840.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Deoxidation of Ferridcyanide of Potassium and of Salts of the Peroxide of Iron. By Prof. SCHÖNBEIN.

WHEN an iron wire with a clean surface is immersed in an aqueous solution of ferridcyanide of potassium, it becomes quickly coated with a layer of prussian blue; and if a number of such wires be placed in a similar solution, there very soon separates a considerable quantity of a bright blue body, which by exposure to the atmosphere acquires a dark blue colour. If into the solution of ferridcyanide air or pure oxygen be passed while it is in contact with the metallic iron, the formation of the blue substance proceeds more rapidly. When finely-divided iron is conveyed into the solution instead of iron wire, and air blown in through a glass tube, the reaction takes place still more rapidly.

However short a time the iron may have remained in contact with the solution of the ferridcyanide, the latter will have become so altered that it is coloured blue when treated with a solution of a persalt of iron.

If the solution be boiled until all the air is expelled from it, and an iron wire, from which likewise the adherent air has been removed by heating in boiling water, be placed in it, the formation of the blue substance around the wire does not occur so long as the liquid is kept boiling, at least not in any perceptible degree. As soon however as the solution is allowed to cool, the metal is seen to envelope itself with a blue coating, *i. e.* if contact between the atmosphere and the solution of ferridcyanide be not prevented.

The solution of ferridcyanide was allowed to boil in a glass flask for ten minutes, and a number of bright iron wires kept in boiling water for the same length of time; the latter were then conveyed as quickly as possible into the boiling solution of ferridcyanide, and allowed to boil for a few minutes, upon which the flask was closed as air-tight as possible. During the first day the wires remained perfectly bright, but on the following day several blue spots were observed on them, the number and size of which became larger and larger, and from which subsequently proceeded minute streaks of a somewhat dirty blue colour. A similar flask was filled with unboiled solution of the ferridcyanide and bright iron wires, and left

open. In a few hours not only had the wires become surrounded with a blue coating, but a large number of the above-mentioned blue streaks were seen to project from the wires into the liquid. The occurrence of these blue streaks is a fact which deserves particular attention, since it appears to prove that the body resembling prussian blue is able to form at places in the solution of the ferridcyanide where there is no metallic iron.

If metallic iron be left sufficiently long in contact with the solution of ferridcyanide of potassium, the latter becomes almost entirely decolorized, and moreover loses the property of forming prussian blue on bright iron. Such a solution affords with pernitrate of iron considerable dark blue precipitates; with the protosulphate of iron, on the contrary, white ones.

Metallic zinc decomposes the solution of ferridcyanide no less rapidly than the iron. If bright laminæ of zinc be placed in an open vessel filled with this solution, yellowish-white points soon appear on them, and after some time a dirty white substance is deposited in the state of a powder at the bottom of the vessel. It consists, according to preliminary experiments, of the cyanide of potassium and zinc, which is probably mixed with some oxide of zinc. If only a trace of this white body be formed, the residuous solution of ferridcyanide is rendered blue by the nitrate of the peroxide of iron, and the precipitate of prussian blue is more abundant when the action of the zinc on the solution of the ferridcyanide has continued for some length of time. The solution, altered in this manner, is also no longer capable of producing prussian blue on bright iron. It is also a very remarkable circumstance that the solution thus altered by zinc disengages ammonia in perceptible quantity when hydrate of potash is added to it, and it is then warmed. In order that the above changes may be effected in the solution of the ferridcyanide of potassium by the zinc, it likewise appears necessary that free oxygen should be present.

When a solution of the ferridcyanide of potassium is brought into contact with arsenic, antimony, bismuth, lead and tin, it is rapidly altered, and is coloured blue with salts of the peroxide of iron. If the contact between metal and solution has lasted only for half a minute, and even at the ordinary temperature, there is nevertheless a perceptible blue colouring produced on the addition of the pernitrate of iron to the solution; and if the metals in question be left for several days in the dissolved percyanide, this will afford considerable precipitates of prussian blue with persalts of iron.

It is remarkable that cadmium acts very slowly on the percyanide, and this metal must have stood for several hours in contact with the solution before the latter exhibits a perceptibly blue tint on the addition of pernitrate of iron. Even copper, mercury and silver effect a change in the solution of the percyanide, and convert a portion of it into the protocyanide. But this reaction proceeds very slowly, and several days' contact is requisite for the solution to become blue on the addition of pernitrate of iron.

A number of the above-mentioned metals lose their lustre (for

instance lead) when placed in the solution of percyanide, and become coated with a film, the chemical nature of which the author has not examined more minutely. It is not improbable that they are compounds of cyanogen, as with zinc and iron. A very easy and simple manner of demonstrating the chemical alteration which the solution of the percyanide undergoes during contact with the above metals, consists in conveying a drop of the liquid to the bright surface of one of the metals, and then adding to it a drop of dissolved nitrate of iron. Immediately after the mixture of the two has taken place, the surface of the metal touched by them is coated with a layer of prussian blue, and the above-described reaction ensues almost instantaneously, even though the metals employed be copper, mercury or silver.

As will appear from subsequent details, the latter metals induce the formation of prussian blue principally from their converting the dissolved persalt of iron partially into a protosalt. The more readily oxidized metals, such as zinc, iron, tin, &c., give rise to formation of prussian blue under the above-mentioned circumstances in a two-fold manner. These metals quickly convert a portion of the percyanide into protocyanide, and a portion of the persalt of iron into protosalt.

The fact that even most carefully-cleansed plates of platinum, palladium and gold produce prussian blue when a mixture of the aqueous solutions of ferridcyanide of potassium and pernitrate of iron is brought on to them, is highly remarkable. It is true that the change in this case takes place very slowly.

We are therefore apparently justified in concluding that all metallic bodies, without a single exception, are capable of producing the same effect on the haloid salt. If the solution of the cyanide be poured over finely-divided protoxide of copper or protoxide of tin, and both substances left only for a short time together, the filtered liquid is rendered strongly blue on the addition of pernitrate of iron. Probably other oxides, which have a greater inclination to combine with more oxygen, behave in a similar manner.

[To be continued.]

On the Atomic Weights of Copper, Mercury and Sulphur. *By* Drs. Erdmann and Marchand.

Copper.—The atomic weight of this element was determined, according to Berzelius's plan, by the reduction of the oxide; the copper employed in the experiment was precipitated by galvanic action from sulphate of copper which had been freed from every perceptible trace of impurity by frequent recrystallization, at first from dilute nitric acid, and then from distilled water; it was dissolved in pure nitric acid, and the nitrate of copper thus obtained decomposed in a platinum crucible by strong ignition over an Argand lamp.

In the first experiments, the pure oxide was ignited over Hess's lamp in a glass tube drawn out at both ends, while a current of dry air was passed over it, which was continued until it had become

completely cooled. The ignited and weighed oxide was then slowly reduced with hydrogen gas, which had been previously conveyed through a solution of oxide of lead in potash, then through sulphuric acid, and at last through a broad and long tube filled with fragments of caustic potash. The water obtained was carefully tested for nitric acid, and was found to be perfectly free. A continuous current of dry atmospheric air was passed over the copper, which had been allowed to cool in the current of hydrogen, the tube and the copper weighed, and the weight corrected for vacuum; the specific weight of oxide of copper being considered as 6·4 and that of the copper 8·9. A reduction of the weights to vacuum was not considered necessary. In two experiments the weighings were made *in vacuo*, the reduction-tube being drawn out only in front to a point, while behind it was provided with a small cock. After ignition the point was sealed, the tube emptied of its air and weighed after closing the cock. The results obtained were—

Corrected.		Weighed in vacuo.	
79·878	79·860	79·873	79·845

The average therefore is 79·86 per cent. Cu, whence the equivalent for copper = 396·6 or 31·7.

Mercury.—To obtain pure peroxide of mercury, commercial mercury was dissolved in pure nitric acid, and the crystallized salt decomposed in a glass retort, the residuary oxide heated in an iron retort to perfect decomposition, and the pure distilled mercury oxidized by treatment with pure nitric acid at a gentle heat. It was found on examination to be entirely free from nitric acid, and left on decomposition by red heat no residue. When oxide of mercury is heated in a retort, a perfectly pure bright metal is never obtained; it is generally semi-fluid, and more or less iridescent, sometimes even covered with a gray film. This is evidently a source of error, which would give too high an atomic weight for mercury; it was avoided in the following manner:—The oxide was first strongly ignited in a current of air, in a glass tube provided with a long downward-curved point, and drawn out posteriorly to a somewhat long neck, until the entire mass began to be decomposed. The heat was gradually increased, and the oxide finally allowed to cool in the current of air, so as to remove every trace of mercurial vapour. On examining the oxide, not a trace of metallic mercury could be detected. When the point of the tube had been freed from mercury and sealed, it was weighed. The decomposition of the oxide was effected in a Bohemian glass tube about 3 feet long, which was drawn out in front to an open point from 9 to 10 inches in length, and curved downwards. A loose stopper of copper shavings, which had been first oxidized by heating them exposed to the air, and had then been reduced in a current of hydrogen, was introduced through the other end, and thrust forward to near the point. This copper was followed by a stratum, 5 to 6 inches in length, of small fragments of strongly-ignited sugar-charcoal, from which every trace of dust had been carefully removed by sifting, and then the oxide was emptied from the first tube, and the latter re-weighed. To advance to the front

every trace of oxide which might have remained adhe
hinder portions of the tube, it was finally rinsed with pulvto the copper; the tube, thus arranged, was treated precisely in the sank manner as in organic analysis, and then placed in a long furnace. To the hinder extremities, a broad tube, filled with chloride of calcium, was affixed by means of a caoutchouc tube; to this was applied a Liebig's potash-apparatus filled with sulphuric acid, and at last a large gasometer filled with carbonic acid. The point in front of the tube was connected by a caoutchouc tube with a weighed recipient destined to receive the mercury. This recipient resembles the potash apparatus figured by Mitscherlich in the last edition of his 'Manual.' The mercury which passes over at the point collects in three bulbs; the arm which ascends from the last bulb is about 5 inches long and three-quarters of an inch broad, and is loosely filled with gold leaf, so as to retain any trace of mercurial vapour which had not been condensed in the bulbs; it is closed above with a cork, which is entirely coated with sealing-wax, into which a narrow tube is fitted to convey away any gas.

When the apparatus has been thus arranged, and it has been ascertained to be air-tight, dry carbonic acid is allowed to pass from the gasometer through the apparatus, and the tube is immediately surrounded with incandescent charcoal, proceeding from the front towards the hinder part in the same manner as in an organic analysis. The carbon in the anterior portion of the tube is seen to burn at the expense of the liberated oxygen, and the mercury which distils over in the current of carbonic acid collects perfectly bright in the recipient. On the combustion of the charcoal, some water is formed, which passes over along with the mercury; this water is entirely removed, as well as the carbonic acid contained in the apparatus, by a current of atmospheric air at the close of the operation; for as soon as all the oxide of mercury is perfectly decomposed, a gasometer filled with air is substituted for the one containing carbonic acid, and the apparatus allowed to cool slowly, while a current of dry air is passed through it. The mercury appears perfectly dry after a short time; the current however is continued for some hours. To be convinced of the entire removal of all moisture from the vessel containing the gold, a weighed chloride of calcium tube is connected with it, and it is seen whether this, after the lapse of half an hour, has retained its primitive weight. The mercury collected in the point is driven as much as possible, with the aid of a spirit-lamp, into the recipient, the point itself sealed as high up as necessary, and first weighed with the apparatus containing the mercury, and after ignition weighed alone in order to deduct its weight from the total. Four experiments gave, corrected for vacuum, 92·594, 92·596, 92·598, 92·596; the mean therefore is 92·596, whence the equivalent for mercury = 1250·9 or 100·07.

Sulphur.—Several experiments convinced the authors that the sulphate of lead parts with sulphuric acid at a red heat, and is therefore useless for the determination of the atomic weight of sulphur. The certainty with which mercury can be determined quantitatively

...ation with oxygen and sulphur, and the ease with which in its crur compound, vermilion, may be obtained in a pure state, ...duced the authors to attempt to determine the atomic weight of sulphur from its combination with mercury.

Commercial vermilion sometimes leaves behind on sublimation traces of a ferruginous non-volatile substance; it may moreover contain mixed with it free sulphur. The authors selected for their experiments an extremely beautiful crystalline vermilion from an old collection of chemical preparations, and also some very beautiful pieces of Dutch vermilion. They were first heated in a current of air until the whole of the intermixed sulphur was driven off, and then submitted to three successive sublimations, taking care to remove the first portion of sublimate, and only employing that which condensed subsequently. The experiments were made with vermilion from three different preparations. The decomposition was effected in an apparatus similar to that employed for the analysis of the oxide of mercury. The anterior portion of the glass tube, drawn out into a long point, was filled for 6 or 8 inches with copper turnings, which had been previously oxidized on the surface and then reduced in a current of hydrogen. The vermilion, freed from any adherent moisture in a current of hot air, and weighed with the drying apparatus, was mixed in a mortar with metallic copper which had been reduced by hydrogen from oxide of copper, filled into the tube, and this, as well as the mortar, carefully rinsed with metallic copper, with which the hinder portion of the tube was likewise filled for several inches. In the last two experiments, the mixture of the vermilion with the metallic copper was effected in the tube itself, by means of a steel wire wound like a screw. The mixture cannot be made with brass wire, as vermilion, on being brought into contact with brass, amalgamates it even in the cold. The mercury was received in the vessel which contained the gold in the preceding experiment. During the decomposition, a current of carbonic acid was passed through the apparatus. The decomposition ensued with the greatest ease and uniformity, and the mercury distilled over perfectly pure and bright, while the sulphuret of copper remained in the tube, confined entirely to the spot where the vermilion was situated. As soon as the operation was finished, any carbonic acid present in the apparatus was expelled by a current of dry air. Four experiments gave 86·212, 86·205, 86·206, 86·222; the mean therefore is 86 per cent. Hg, whence follows that if Hg = 1250·9, the atomic weight of sulphur must be 200·07 or 16·002.—*Journ. für Prakt. Chem.*, xxxi. p. 385.

On Carbonate of Ammonia and Magnesia, Carbonate of Ammonia and Zinc, and Carbonate of Magnesia. *By* M. Favre.

Carbonate of Ammonia and Magnesia is obtained on agitating a solution of carbonate of ammonia with carbonate of magnesia. The filtered solution deposits small rectangular prisms, which are easily dried, and may be preserved unaltered in closed bottles. This salt

contains 16·2–16·3 per cent. magnesia. It is rendered turbid by treatment with cold water, and then contains 29·3 magnesia and 38·7 water, like neutral carbonate of magnesia. On boiling it for any length of time in water, it is converted into a light mass, which contains 44·2–44·61 magnesia and 21·4–21·64 water; it has therefore the composition of *magnesia alba.* A similar powder is deposited on boiling the mother-ley separated from the double salt. The double salt is insoluble in pure water, but somewhat soluble in carbonate of ammonia. It may readily be obtained in a crystalline state by digesting *magnesia alba* in carbonate of ammonia, when the magnesia gradually becomes entirely converted into granular crystals of the double salt. It is however obtained most beautifully crystalline by mixing a saturated solution of bicarbonate of magnesia with a solution of carbonate of ammonia.

The analysis of the crystals gave—

				Equiv.	Calc.
MgO	15·92	15·77	15·8	1	16·28
CO^2	34·00	34·90		2	34·70
Hydrogen.....		6·70		8	6·31
Nitrogen		11·60		1	11·17
Oxygen.....				5	31·54

$= CO^2, MgO + CO^2, NH^4O + 4$ aq.

Carbonate of Zinc and Ammonia.—When recently precipitated carbonate of zinc is edulcorated with a solution of carbonate of ammonia, the filtered liquid deposits, according to circumstances, either rectangular prisms or needles in stellate groups; sometimes the whole mass on the filter is converted into them. The best crystals are obtained by continuing the edulcoration until the liquid in the glass cylinder reaches the margin of the funnel, and then placing in the filter containing the excess of carbonate of zinc a few solid pieces of carbonate of ammonia. In this manner the liquid constantly remains saturated during its slow evaporation and crystallization; when the level of the liquid has sunk to the extremity of the funnel, the latter will be found to be filled with beautiful crystals of the double salt. A few more pieces of carbonate of ammonia are now added to the filtered liquid, which is then left to spontaneous evaporation. The crystals consist of—

ZnO	57·7	56·7	57·24	2	56·9
CO^2	30·80	31·0		2	31·1
Hydrogen.....		2·6		3	2·1
Nitrogen		10·2		1	9·9

$= CO^2, ZnO, + CO^2\ ZnO\ NH^3.$

The author regards the second member as a combination of carbonic acid with an oxide of ammonium in which an equivalent of hydrogen is replaced by zinc. The salt slowly becomes opake in cold water, and passes into basic carbonate of zinc, retaining however the form of crystal. The same is effected more rapidly by boiling in water, when the carbonate of zinc is obtained in the state of powder, and contains 73·1–74·38 oxide of zinc, 11·83–12·22

water; the formula 3ZnO, 1 and $\frac{1}{2}CO^2$ + ZnO, 3HO requires 73·0 oxide of zinc and 12·1 water. The double salt is readily soluble in carbonate of ammonia; it is not altered by exposure to the air nor by boiling with alcohol. By heating it carefully, a white sublimate of anhydrous carbonate of ammonia is obtained (the analysis afforded 55·8 CO^2 and 8·0 H).

Carbonate of Magnesia.—When sulphate of magnesia is precipitated in the cold with carbonate of soda, no liberation of carbonic acid ensues. If as little water be used as possible, the first precipitate (I.) is neutral carbonate of magnesia; and even after washing three times with boiling water, it still continues to be the neutral salt (II.). The liquid filtered from this precipitate deposits some minute crystals, which are likewise the neutral salt (III.); and the liquid separated from this deposits on boiling a small quantity of basic salt (*magnesia alba*). If the precipitate be dissolved in water impregnated with carbonic acid, the solution again deposits on standing crystals of the neutral salt.

	I.	II.	III.	IV.		
MgO	29·66	29·39	29·5	29·38	1	29·58
CO^2					1	31·51
HO	39·33	39·28	38·7	38·97	3	38·91

It is therefore certain that originally only neutral salt is formed on the precipitation of sulphate of magnesia with carbonate of soda; but a larger or smaller portion may be decomposed by the water, and thus *magnesia alba* become mixed with the precipitate; the liberated carbonic acid remains in the liquid, and dissolves a portion of the neutral salt.—*Ann. de Chim. et de Phys.*, t. x. p. 474.

ANALYTICAL CHEMISTRY.

On Chlorine and Sulphocyanide of Potassium as Tests for the Vegetable Alkaloids. By M. Lepage.

In the experiments instituted for the purpose of ascertaining the behaviour of these reagents towards the alkaloids, the author employed a solution of $1\frac{1}{2}$ gr. of alkaloid in about 10 drms. distilled water, with 1 or 2 drops of sulphuric or hydrochloric acid: a current of chlorine gas passed through this solution for ten minutes gave rise to the following reactions:—

Strychnine.—No colour; after five minutes a milky turbidness, and finally formation of a sediment.

Brucine.—Pale red colour, which on further treatment with chlorine again disappears; no opacity.

Morphine, Narcotine and Emetine (the latter not quite pure).—A saffron-yellow colour, which does not disappear. With the emetine there is at last a formation of a deposit.

Quinine, Cinchonine and Veratrine.—Neither colour nor opacity.

Chlorine accordingly is very applicable for the detection of strychnine, and for ascertaining the presence of any brucine in it, and *vice versâ* of any strychnine in brucine. The precipitate formed with strychnine is insoluble in water, even when acidulated, and in æther; but it is soluble in alcohol. The reaction is very sensitive.

Solutions of the alkaloids, prepared in the same manner, but treated with a slight excess of a solution of sulphocyanide of potassium, gave rise to the following reactions:—

Strychnine.—A gradual separation of beautiful long acicular crystals when undisturbed; on agitation, immediate formation of a crystalline precipitate.

Brucine.—After twelve to thirty-six hours a white granular crystalline precipitate; on stirring, immediate separation of a crystalline powder.

Cinchonine.—Frequently no opacity when undisturbed; on agitation, a deposit of crystalline laminæ, very similar to the protoxide of mercury.

Quinine.—In twelve to thirty-six hours a greenish-yellow precipitate, consisting of minute acicular crystals; on agitation, almost immediate deposit of a greenish-yellow powder.

Veratrine and Emetine.—Pulverulent precipitates, soluble in an excess of the alkaloid.

Morphine and Narcotine.—No reaction, not even on stirring.

All the precipitates above-mentioned, which appear to be double salts, are soluble in water and alcohol, but insoluble in æther, except when the alkaloid itself is soluble in æther. They all dissolve in nitric acid with a transitory wine colour, with the exception of the brucine compound, which becomes blood-red, and is rendered violet by protochloride of tin.

The reactions with strychnine, quinine and cinchonine are accordingly the most characteristic. The precipitate with strychnine has moreover this peculiarity, that its aqueous solution is decomposed by chlorine, with formation of the above-described white deposit.—*Journ. de Pharm.*

On a new Method for the Quantitative Determination of Copper. *By* Prof. Brunner.

In quantitative analysis the precipitate obtained in a solution of copper with sulphuretted hydrogen is generally redissolved in acid, and this solution employed to determine the oxide of copper by a second operation. This process is adopted in order, without doubt, to avoid taking into account any sulphur which may have become mixed with the sulphuret through some secondary action. To ascertain exactly what takes place in this operation, I precipitated the copper from a solution of the sulphate by passing into it sulphuretted hydrogen; I washed the precipitate with water containing sulphuretted hydrogen in solution, and after having pressed the mass in folds of blotting-paper, dried it in a current of dry air at 212°. I then treated 2·948 grms. in a flask with fuming nitric acid until

the undissolved sulphur appeared perfectly pure. Its weight, after washing and drying, was 0·36 grm. I then mixed this solution with some hydrochloric acid, boiled it for some time, and after diluting it with water, precipitated the sulphuric acid by chloride of barium. The precipitate after calcination weighed 5·031 = 0·6941 sulphur; the entire proportion of sulphur therefore amounted to 1·055, or to 35·787 per cent.

A sulphuret of copper which would be represented by the formula CuS should contain 33·705 per cent. sulphur. It is evident therefore that a mixture of sulphur is contained in the precipitate.

Since it is possible to remove by heat a portion of the sulphur from a sulphuret composed according to the above formula, I tried whether it would not be possible to obtain by this means an exact method which would be applicable in chemical analysis to the determination of copper; for this purpose I conveyed into a tube with a bulb a certain quantity of sulphuret of copper prepared according to the above process, passed a moderate and continuous current of hydrogen gas over it, after which I heated the sulphuret of copper with a spirit-lamp as long as sulphur was liberated. I then allowed it to cool in a current of gas. 1·547 of the sulphuret of copper thus obtained, analysed by the same method as the preceding, afforded 0·019 of undissolved sulphur and 2·109 sulphate of barytes (= 0·290978 sulphur), altogether 0·30997 sulphur, or 20·037 per cent. A combination, the formula for which would be Cu^2S, should contain 20·268 per cent. sulphur. Consequently the precipitate of sulphuret of copper, treated with hydrogen, may serve for the determination of copper as well as the oxide. Perhaps this new process would even present the advantage of occupying less time.—*Bibliothèque Univ.*, May 25, 1844.

CHEMICAL PREPARATIONS.

On the Preparation of the Lactate of Lime. By M. Gobley.

The principal use of the lactate of lime is for the preparation of the lactate of iron, a substance which at present is much employed in medicine. The high price demanded in the course of last year (16 shillings the lb.) by the manufacturers induced me to prepare some. For this purpose I adopted the ingenious process which MM. Boutron and Fremy have given in their memoir on lactic fermentation. This process does very well, but the product comes to a high price. Being persuaded that it might be rendered less expensive, I have modified it in several ways, and finally arrived at the following:—

Some small porcelain tureens, holding about 3 quarts, are filled with 250 grms. of powdered milk-sugar, 200 grms. of pulverized chalk, a quart of skimmed milk, and sufficient water to fill them. These vessels are then exposed in a situation the temperature of

which is from 77° to 86° Fahr., agitated from time to time, and the water replaced in proportion as it evaporates.

After 24 hours' contact fermentation begins to be perceptible; carbonic acid is disengaged, especially on agitation, during the whole time the fermentation lasts; it terminates about the eleventh or twelfth day; when however 2 quarts of milk are taken instead of 1, fermentation ceases towards the ninth or tenth day. During the first days the mixture possesses the odour of sour milk, but towards the conclusion a faint odour of cheese. The end of the fermentation is evidenced by the liquor, in which the powders were readily suspended, by agitation being as it were solidified; it forms a liquid, in which a large quantity of curds float. When well-skimmed milk is used, no butyraceous matter separates during the first days; but when the liquid has become more dense, from the lactate it holds in solution, a small quantity always floats on the surface.

The product of the lactic fermentation is conveyed into a dish, and slowly heated to boiling, stirring the whole time; without this precaution the deposit would adhere to the bottom of the vessel, and communicate a disagreeable odour to the liquid. It is boiled for a quarter of an hour to coagulate the caseum, allowed to subside, and filtered through flannel; the deposit is washed with boiling water, to separate the lactate of lime which it retains, and the wash-water added to the first liquor. The liquid is now filtered, after having added more water to it, the quantity present not being sufficient to hold the lactate in solution; and then, if it be desired to separate the lactic acid, it is decomposed with oxalic acid; otherwise, to obtain the lactate of lime, it should be evaporated at a *gentle heat* to about one-third. After 24 hours' rest, a mass of lactate of lime is obtained, which is folded in linen and submitted to the action of a strong press, in order to separate it as much as possible from the fluid adhering to it; the cake is then broken, and placed to dry in the hot chamber. The mother-liquor, evaporated and treated in the same manner, affords a further quantity of lactate of lime. The residue of these operations is a soft, coloured, fatty and gelatinous matter, which is thrown away.

The lactate of lime thus obtained is very pure, perfectly white, and in the shape of fragments, formed by the union of small globules, which is the crystalline form peculiar to the lactate of lime, and which is a very good character by which to ascertain its purity.

The process of MM. Boutron and Fremy, modified as above, is very œconomical; for with a quart of skimmed milk and 250 grms. of sugar of milk, about 340 grms. of lactate of lime are obtained, which does not come to 2*s.* 6*d.* the lb.

I attempted to prepare the lactate of iron by an analogous process. With this view I placed some skimmed milk, milk-sugar and an excess of iron filings in a large flask, and left the mixture to itself in a warm place, taking care to agitate it from time to time. The action was at first slow; subsequently it became more active. In this case the hydrogen of the decomposed water was liberated at the same time that the oxygen combined with the iron, and the

oxide entered into combination with the lactic acid which had formed. The liquor possessed the green colour of the protosalts of iron, and preserved it to the end of the fermentation. There now only remained to separate from the liquid the lactate of the protoxide of iron it contained; but on evaporating it, even over iron filings, it became yellow, and the product was no longer lactate of the protoxide of iron. Perhaps on studying this process more minutely, we may succeed in obtaining directly lactate of iron of good quality, which would considerably lessen the price.

Although the lactate of lime does not bear a high price with the process previously described, I have nevertheless endeavoured to obtain it at a cheaper rate. For that purpose I submitted to the combined influence of caseum and carbonate of lime substances of less value than milk-sugar, and which like it are composed of carbon, oxygen and hydrogen, in the proportion to form water. These substances are gum, starch, sugar and dextrine.

Dextrine.—I placed in a small porcelain tureen 2 quarts of skimmed milk, 1 pint of water, 250 grms. of dextrine and 200 grms. of pulverized chalk. The tureen was then placed in a situation the temperature of which was from 77° to 86°, and the water was replaced as it evaporated. At the end of 10 days I stopped the fermentation by boiling the whole; the strained liquid, evaporated and then left for 24 hours, gave a very perceptible quantity of lactate of lime. The whole of the dextrine was not converted after 10 days' fermentation into lactic acid. I was therefore not able to ascertain the quantity of lactate of lime which 250 grms. of dextrine would furnish. The lactate of lime obtained was of very excellent quality.

Sugar.—I placed in a tureen 250 grms. of lump-sugar, 2 quarts of skimmed milk, 1 pint of water and 200 grms. of pulverized chalk. When such a mixture is kept at a temperature varying between 59° and 77° Fahr. it becomes thick, and this thickening increases in such a manner that at the end of 5 days it resembles a thick soup; the sweet taste has then entirely disappeared. The fermentation still continues, but no peculiar sign indicates its termination.

After 10 days I discontinued the fermentation by boiling; the liquid, strained and evaporated to a third, gave after 24 hours' rest a large quantity of lactate of lime. This lactate was submitted to pressure; the liquid obtained from it, evaporated and left to itself, gave a further quantity of lactate, which however was mixed with a thick, highly viscid mass. This substance, separated from the lactate of lime, and treated several times with alcohol, became converted into a tolerably solid spongy gray substance, insoluble in alcohol but soluble in water. According to MM. Pelouze and Gelis, it is the intermediate substance between sugar and lactic acid, and is composed of $C^{12} H^{10} O^{10}$.

When the preceding mixture is placed in a situation the temperature of which is from 77° to 86° Fahr., it thickens much less; I have even once seen it scarcely happen at all, and then noticed that the fermentation terminated much sooner. The temperature appears therefore to exert great influence upon this phænomenon, which

MM. Pelouze and Gelis have designated by the name of viscid fermentation. This viscosity is sometimes developed, although in a less degree, during the fermentation of milk-sugar. I have remarked it under two circumstances;—1st, when the fermentation is carried on at a low temperature, although the quantity of ferment is pretty considerable; 2nd, when the quantity of ferment is small, notwithstanding that the temperature is from 77° to 86° Fahr. This viscosity is especially apparent when some of the deposit is raised and let fall with a spatula.

If into the mixture exposed in a situation where the temperature is from 77° to 86° Fahr. the water is replaced as it evaporates, no sign indicates when the fermentation ceases; but if it is not replaced, the liquid becomes so concentrated that the whole of the lactate produced cannot remain in solution, and then towards the eighth day it congeals into a mass, as happens with the milk-sugar. 250 grms. of sugar afforded 280 grms. of lactate of lime.

Sometimes during the fermentation of the sugar a disagreeable odour is developed, which however is not persistent. I have not known to what to attribute it, for it was not manifested in a mixture made with the same substances in similar proportions and placed in the same circumstances. I have never remarked this odour during the fermentation of milk-sugar.

It is important that the lactic fermentation should not be prolonged beyond the time we have indicated, nor should it be allowed to languish in order to avoid the transformation of the lactate into the butyrate of lime; for, as shown by MM. Pelouze and Gelis, butyric fermentation not only succeeds the lactic, but likewise these two fermentations, instead of being successive, may be simultaneous.

Starch.—I placed in a tureen 2 quarts of milk, a pint of water, 250 grms. of powdered starch, and 200 grms. of pulverized chalk. The mixture was exposed in a situation at a temperature of 77° to 86°, the water replaced as it evaporated, and now and then agitated; the fermentation was very lively after 24 hours. During the first days the starch formed a thick layer at the bottom of the vessel, but subsequently dissolved. There is probably formed in this case an intermediate substance, analogous to that which is produced during the fermentation of sugar. The liquid however does not become viscid, nor does it give off any disagreeable odour. I interrupted the fermentation at the end of 20 days, and the liquid, treated like the preceding, gave a large quantity of beautifully-white lactate of lime. I am not able to say how much 250 grms. of starch are capable of producing, the fermentation having been discontinued before it was concluded. Undoubtedly potato-starch would behave in the same manner under the combined influence of caseum and carbonate of lime.

Gum, treated in the same manner, gave but a very small portion of lactate after 10 days' fermentation.

I likewise ascertained by experiment, that under the influence of carbonate of lime and of beer, yeast, milk-sugar, cane-sugar, dex-

trine, starch and gum undergo lactic, and subsequently butyric fermentation.

With respect to the processes for the preparation of the lactate of lime, those with milk-sugar and cane-sugar appear to me most advantageous. Although the lactate obtained from cane-sugar is cheapest, that furnished by milk-sugar will be preferred from its superior quality, and because the fermentation is easy to conduct. The lactate obtained with milk-sugar is whiter and in larger globules.

The process with starch is not to be despised, and I doubt not, from the low price of the material and the excellent product it affords, that it will be found profitable to substitute it for the starch-sugar proposed by MM. Pelouze and Gelis in the manufacture of this article.—*Journ. de Pharm.*, July 1844.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Source and Nature of Colouring Substances of Organic Origin, and on the Action of Oxygen upon them. By F. Preisser.

[Continued from page 395.]

Carmine.

The colouring principle of the cochineal was isolated in the year 1818 by MM. Pelletier and Caventou*, who gave it the name of *carmine*. They obtained it by exhausting cochineal with æther, which removes all the fat matter, treating the residue at several intervals with boiling alcohol, allowing it to cool, redissolving the deposit, which forms in pure cold alcohol, and then adding an equal volume of pure hydrated æther. The carmine is deposited in purple-red crystalline granules. In 1819 M. Lassaigne also found this principle in the kermes, *Coccus ilicis*†; and it is probable that it equally exists in all the other species of *Coccus* which also furnish tinctorial matters, such as the *cochineal* or the *kermes of Poland*, the *gum or resin lac* of commerce. In 1832 Pelletier submitted carmine to elementary analysis, and assigned to it the formula $C^{16}H^{18}O^{10}$; but he adopted this formula with some hesitation, supposing that the matter retained a little water, from its being very difficult to dry without decomposition‡.

To obtain carmine in a pure state, good cochineal is digested with æther to free it from all fat matters, and then a strong decoction

* "Examen chimique de la Cochenille et de sa Matière colorante."—*Journ. Pharm.*, t. iv. p. 193. *Ann. de Chim. et de Phys.*, t. viii. p. 250.

† Lassaigne, "Examen chimique du kermes végétal."—*Journ. Pharm.*, t. v. p. 435. *Ann. de Phys.*, t. xii. p. 102.

‡ Pelletier, "Recherches sur la Composition élémentaire de plusieurs Principes immédiats des Végétaux."—*Ann. de Chim. et de Phys.*, t. lxi. p. 194.

made with water. Hydrate of lead entirely precipitates the colouring principle, and the supernatant liquor is rendered perfectly colourless. The violet carminate of lead is decomposed by an excess of sulphuretted hydrogen, and the nearly colourless filtered liquid deposits on cooling small needles of a pale yellow, which become entirely white on edulcoration with æther and pressure between folds of blotting-paper.

Carmine is colourless, of a somewhat disagreeable nauseous taste. It is soluble in water and in alcohol, much less so in æther. It becomes coloured slowly by contact with the air; its solution becomes reddish-yellow round the edges. When boiled it becomes coloured, and on concentration deposits a quantity of beautiful purple-red flakes of *carmeine*.

The colourless solution of carmine, heated in a small retort with some bichromate of potash, affords a liquid of a beautiful red colour, which soon deposits a quantity of red flakes of a compound of carmeine and oxide of chrome. This lake is decomposed by caustic potash, the oxide of chrome being left in the form of a yellow powder.

Mineral acids redden carmine, especially nitric acid, and dissolve it; alkalies turn it immediately into a violet-red colour, more or less dark, and at the same time the colouring matter is for the greater part deposited.

Acetate of lead gives a white precipitate, which turns blue in the air, and becomes of a dark bluish-violet when shaken.

Carmine and carmeine are not of themselves volatile; a small portion of the red matter is merely carried away by the vapours of the portion which is decomposed. Both furnish ammoniacal products by their decomposition.

II. Yellow Principles.

Quercitrine.

M. Chevreul has given the name of *Quercitrine* to the principal colouring matter of the bark of the quercitron (*Quercus nigra*, L., *Quercus tinctoria*, Michaux). He obtained it in small laminæ or scales, of a pale grayish yellow, by slowly concentrating an infusion or decoction of the bark, and leaving it to cool. According to this chemist, this substance is accompanied in the bark by a red colouring principle, by a brown principle and by tannine. The first two substances owe their origin, in part at least, to the alteration of the quercitrine*. The stale decoction of quercitron gives but a small quantity of dye; the greater part of the quercitrine is deposited, and what remains in solution is of a dark colour, and does not fix so well upon stuffs.

In 1840 M. Bolley instituted some experiments on the yellow colouring principle of the quercitron. He obtained it by exhausting the pulverized bark with alcohol of 84° in a displacement apparatus,

* Chevreul, "Leçons de Chimie appliquée à la Teinture," 30e leçon, t. ii. p. 162.

precipitating the tannine by gelatine or by a little lime, and evaporating the filtered liquid. Yellow crystalline crusts are deposited. They are purified by washing with water, then dissolving them frequently in alcohol, adding some water, and evaporating the solution, which finally affords a crystalline powder of a sulphur, or even chrome-yellow colour. Bolley applied the name of *quercitric acid* to this substance, because it reddens litmus perceptibly and combines with bases*. He represents it by the formula $C^{16} H^8 O^9 + HO$, and its lead salt by $C^{16} H^8 O^9 + PbO$.

We obtained *quercitrine* in the following manner:—A small quantity of gelatine was at first added to the aqueous decoction of quercitron, so as to precipitate all the tannine. The filtered liquid was then treated with a very small quantity of hydrate of lead, which produced a dirty brown precipitate. The decanted liquor was of a very beautiful golden-yellow colour, and afforded an abundant precipitate of a brilliant yellow colour on the addition of hydrate of lead.

This last lake, when well washed and decomposed by a current of sulphuretted hydrogen, afforded a colourless liquid, which on evaporation *in vacuo* gave white needles of pure quercitrine.

Quercitrine is colourless, and has at first a slightly sweet, subsequently a bitter taste. It is very soluble in water, in alcohol and in æther. In contact with the atmosphere it gradually becomes of a bright yellow, and by degrees the solution deposits yellowish-white flakes, of a crystalline appearance. The aqueous solution, if left a long time in contact with air, acquires a dark yellow colour.

Mineral acids dissolve it, giving it a yellow colour. Alkalies, in contact with the air, turn it of a dark brown yellow. Ammonia produces the same effect. Lime-water immediately changes its colour to a brown yellow; acetate of lead affords a white precipitate, which may be dried in a tube filled with nitrogen, without becoming perceptibly coloured; but by exposure to the atmosphere, it acquires a yellow tint after a few hours.

On boiling a solution of quercitrine, it becomes turbid, and deposits a quantity of small acicular crystals of *quercitreine*, less soluble in water, and which forms with hydrate of lead a beautiful golden-yellow lake of lead, *quercitreate*.

These facts therefore show, that in the bark of the quercitron there is but one colouring principle, colourless in the heart of the wood, and which only passes into the state of a yellow principle, or *quercitreine*, by the absorption of oxygen from the atmosphere. The brown principle of the wood is a mixture of quercitrine and of tannine, or rather of quercitreate of lime coloured brown by altered tannine.

Quercitrine and quercitreine are for the greater part volatile. They contain no nitrogen.

The yellow quercitreate of lead consists of—

* Bolley, Ann. der Chem. und Pharm., xxxvii. p. 101. Rapport Annuel de Berzelius, de 1841, p. 116.

	Found.	Equiv.		Calculated.
Carbon	41·53	32	= 2400·0	41·5
Hydrogen	3·33	15	187·5	3·2
Oxygen	31·20	18	1800·0	31·2
PbO	23·94	1	1394·5	24·1
	100·00		5782·0	100·0

and the colourless quercitrate of lead of—

Carbon	51·11	32	= 2400·0	50·1
Hydrogen	3·99	15	187·5	4·0
Oxygen	29·84	14	1400·0	31·0
PbO	15·06	½	697·2	14·9
	100·00		4684·7	100·0

The formula for the quercitrate of lead should consequently be represented by $2(C^{32}H^{15}O^{14}) + PbO$, and its atomic weight by 4684·7. It is evident therefore that quercitrine, on changing into quercitreine, absorbs 4 atoms oxygen, and requires twice the quantity of oxide of lead for its neutralization.

Luteoline.

M. Chevreul is the only chemist who has paid attention to the yellow colouring matter of the woad. He obtained it by sublimation, in small needles of a pale yellow colour, and gave it the name of *luteoline**. According to him, this matter does not represent all the tinctorial properties of the woad, for this imparts a reddish substance to the stuffs, which tarnishes the brilliancy of the luteoline. A considerable quantity of this reddish matter exists in the dry woad, but it may be produced from it at the expense of the luteoline, when the infusion or decoction of woad is exposed for any length of time to heat in contact with air†.

On applying the same process to the decoction of woad as for the other tinctorial substances, a bright yellow liquid is obtained, which on cooling deposits a quantity of spangles of yellowish-white colour. When this liquid is boiled with a few drops of syrupy chromic acid, or a small quantity of bichromate of potash, we obtain on cooling large laminæ of a beautiful golden yellow, exactly similar to the iodide of lead. These laminæ are likewise obtained without the aid of oxidizing agents, by long contact with the atmosphere. We shall call this yellow principle *luteoleine*.

Luteoline forms white spangles, which are soluble in water, but much more so in hot than in cold; they are also soluble in alcohol and in æther.

It has at first a sweetish, subsequently a slightly bitter taste. It is volatile, and sublimes in needles of a golden yellow, mixed with others having less colour. It has a distinctly acid reaction.

* Chevreul, "Leçons de Chimie appliquée à la Teinture," t. ii. 30ème leçon, p. 143.

† Chevreul, "Généralités sur la Teinture."—*Dictionn. Technologique*, t. xxi. pp. 387 and 415.

Sulphuric acid turns it of a bright yellow, and dissolves it. Nitric acid imparts to it a darker yellow tint more rapidly; and if heated, there is disengagement of reddish vapours.

The protosulphate of iron precipitates it of a very pale greenish yellow; but on exposing the precipitate to the air, it grows darker, and becomes olive brown. Acetate of lead gives a white precipitate, which turns yellow on being kept for a long time in the air.

Potash, soda, ammonia, change the solution of luteoline to a beautiful dark yellow, and after twenty-four hours the liquid has deposited all the colouring matter.

Barytes, strontia and lime water behave in the same manner.

Woad contains tannic acid, which, by becoming coloured in the air by the absorption of oxygen, forms the reddish matter which M. Chevreul found in the decoction of woad.

Morine.

M. Georges and M. Chevreul are, so to say, the only chemists who have examined the *yellow wood*, or Fustic (*Morus tinctoria*, L., and *Broussonetia tinctoria*, Kunth), in a chemical point of view. The former gave an unsatisfactory analysis of this wood*, but the latter described the principles to which it owes its tinctorial properties. M. Chevreul says that two colouring principles exist in the yellow wood capable of dyeing alumed stuffs yellow; he has called them *yellow morine* and *white morine*. Both sublime in crystals. They are distinguished by the aqueous solution of the *yellow morine* becoming green with persulphate of iron, whilst that of the *white morine* turns chestnut-red. *White morine* exists principally in the powder which is found in the interior of the wood. The *yellow morine* is obtained by exhausting the wood with water, evaporating the extract until on cooling it deposits crystals, dissolving these in æther, and evaporating anew. These two principles are easily altered by the air, by exposure to which they acquire a reddish tint†.

All our experiments on the colouring principles have led us to admit that *white morin* and *yellow morin* are only modifications of one and the same principle. In fact, on adopting the same process of extraction as for the other colouring matters, we obtained white morin, which we shall hereafter call *morine*, similar in every respect to the crystalline powder which exists in the heart of the yellow wood, only in brilliant crystals of a very pale yellowish white.

The crystals have a laminar structure. Their flavour is sweet and bitter.

Morine is soluble in water; but the solution absorbs oxygen in contact with the air, acquires a yellow colour, and is transformed into *yellow morine*, which we shall call *moreine*. This took place under a bell-glass, containing pure oxygen, placed over mercury; a considerable quantity of the gas was absorbed, and the solution assumed a golden yellow tint.

* Georges, quoted by Berzelius, Traité de Chimie, t. vi. p. 33.

† Chevreul, "Leçons de Chimie appliquée à la Teinture," t. ii. 3ième leçon, p. 150.—*Dictionn. Technologique*, xxi. pp. 388 and 417.

Mineral acids dissolve morine, imparting to it a yellow colour. Persulphate of iron colours it garnet red, as M. Chevreul had already observed. Acetate of lead precipitates it of a white colour. Submitted to the action of heat in a glass tube, morine sublimes in part in the form of small needles of a pale yellow colour. Alkalies and contact with the air cause it to take a beautiful dark yellow, approaching to orange.

When morine is boiled in water, it absorbs oxygen from the atmosphere, and is changed into *yellow moreine*, which is deposited on cooling. The same result is obtained, and in less time, on oxidizing morine by means of a small quantity of chromic acid or of bichromate of potash. Both afford moreine and oxide of chrome.

Moreine crystallizes in beautiful yellow laminæ, bearing some resemblance to luteoleine. They are volatile. It is perceptibly acid to litmus-paper, and is not very soluble in cold, but much more so in boiling water. It is very soluble in alcohol and in æther. Acids dissolve it, and turn it of a darker colour. Nitric acid colours it brownish-red, giving off red vapours. Alkalies turn it orange. Acetate of lead precipitates it of a golden yellow; persulphate of iron of a dark green colour.

Moreine, in crystals or in solution, is not very permanent. After a time it absorbs a further quantity of oxygen, and becomes reddish-brown. This absorption of oxygen is perceptible when the solution is brought into contact with oxygen over mercury. This is the origin of the red and brown principles which always occur in decoctions of yellow wood, and which exist at the surface of the yellow wood when it has been exposed to the air and light for any length of time.

[To be continued.]

PATENT.

Patent granted to John Barnes, Church, Lancaster, *and* John Mercer, Oakenshaw, Lancaster, *for certain Improvements in the Manufacture of Articles used in printing and dyeing Cotton, Silk, Woollen, and other Fabrics.*

This invention consists in the manufacture of a new material, termed by the patentees "assistant mordant liquor," which, when combined in certain proportions with the ordinary mordants, renders them more effective and useful, thereby improving the manufacture of such articles. The manner in which the improvements are carried into effect is as follows:—

To 100 lbs. avoirdupois of potato-starch add 37½ gallons of water, 12½ gallons of nitric acid of commerce (spec. grav. 1·300), and 4 oz. avoirdupois of oxide of manganese. The chemical action which takes place among these ingredients is allowed to proceed until the nitric acid is destroyed. To the residuum thus produced add 50

gallons of pyrolignic acid, and the compound is the assistant mordant liquor, in a fit state to add to the various mordants used in printing and dyeing. The proportion in which the assistant mordant liquor must be added to produce the various improved mordants, will vary according to the chemical properties and nature of the mordant to which it is applied; but, by experience, the following proportions have been found to produce a greatly improved article:—For black, take 1 gallon of iron liquor (pyrolignate of iron, well known in the arts), 1 gallon of assistant mordant liquor, and 1 gallon of water, either thickened or not, according to the mode in which it is to be applied. For purple, take 1 gallon of iron liquor, 2 gallons of assistant mordant liquor, and 6 gallons of water; for paler purple, 1 gallon of iron liquor, 3 gallons of assistant mordant liquor, and 12 gallons of water; and for still paler purple, 1 gallon of iron liquor, 4 gallons of assistant mordant liquor, and from 20 to 30 gallons of water. These improved articles or mordants are applied, washed and dyed in the usual way. For tin or aluminous mordants the same rule is followed; excepting that red liquor, or other salts of alum, or muriate of tin, or other salts of tin, are used, instead of iron liquor, or other salts of iron. For dyeing silk or woollen, the assistant mordant liquor is added to the tin, iron or aluminous mordant, either with or without colouring matter, in the same boiler; but this, and other practical arrangements, must depend on the judgement and skill of the operator. Having described one process by which assistant mordant liquor is produced, and the manner in which it may be compounded with ordinary mordants, for the purpose of improving the manufacture of such articles, the patentees state that they do not confine themselves to the use of nitric acid in the manufacture of assistant mordant liquor, as the same result may be obtained by the use of other oxidizing agents; such, for instance, as chromic acid and its salts, or the oxides of manganese, along with a mineral acid. Nor do they limit themselves to any exact proportions of acid, or other ingredients; their intention being to carry on the decomposition as far as possible without forming oxalic acid, and as little as possible of carbonic acid, in the process, which is greatly aided by the catalytic action of the manganese, preventing the formation of oxalic acid; and although potato-starch has been found to answer well in the process already explained, yet other starchy, saccharine or gummy substances may be employed; indeed, all substances which contain little nitrogen, and where the oxygen and hydrogen are in the proportion to form water, or nearly so.—Sealed Nov. 10, 1842.

THE CHEMICAL GAZETTE.

No. XLVII.—October 1, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Deoxidation of Ferridcyanide of Potassium and of Salts of the Peroxide of Iron. *By* Prof. Schönbein.

[Continued from p. 399.]

But it is not only the metallic bodies or certain metallic compounds which are capable of exerting a chemical influence of the kind previously described on the solution of the ferridcyanide, but a series of non-metallic substances likewise exhibits a similar behaviour. If phosphorus be held for some length of time in contact with the solution of the percyanide, the latter acquires the property of becoming blue (only indeed in a faint degree) on the addition of a solution of peroxide of iron. But if a piece of phosphorus be held in a mixture of percyanide and solution of a persalt of iron, and be allowed to remain for some time in the liquid or exposed to the atmosphere, it becomes surrounded with a coating of prussian blue. This phænomenon appears however to be principally owing to the persalt of iron being partially converted by the phosphorus into a protosalt. Schönbein passed pure hydrogen gas for some length of time into the solution in question; it appeared however to undergo no change whatever in its chemical constitution under these circumstances. But when the hydrogen came into contact with the dissolved percyanide, either in a nascent state or in certain chemical combinations, it had a different action. If two vessels, communicating with one another by means of a porous septum, for instance animal membrane, be filled with the dissolved cyanide, and the conducting wires of a somewhat powerful battery be conveyed into the liquid of these vessels, a portion of the solution of the percyanide in which the negative electrode is immersed, *i. e.* in which hydrogen is separated, is rapidly changed, and affords a blue precipitate with pernitrate of iron.

Hydrogen combined with sulphur, selenium, phosphorus, arsenic, antimony and tellurium, although still gaseous in these combinations, acts nevertheless very rapidly on the solution of the ferridcyanide, and indeed in a similar manner to nascent hydrogen. If either one of the last-mentioned gases be passed for only a short time into the solution of the cyanide, it is so much altered by it that it affords blue precipitates with persalts of iron, even after the expulsion of

any gas dissolved in the liquid. If the solution of cyanide, before being submitted to the action of any of these hydrogen compounds, be mixed with a solution of the pernitrate of iron, a very considerable precipitation of prussian blue takes place on the entrance of the gas into the mixture. It must however be observed that the three first-mentioned gases act far more rapidly than the three metallic hydrogen compounds are capable of doing.

If the solution of cyanide be allowed to stand with æther or alcohol for ever so long, it does not appear that the mixed substances act on one another under these circumstances, since a solution thus treated is not rendered perceptibly blue on the addition of a persalt of iron. But if, besides the æther or alcohol, some nitrate of iron be added to the dissolved cyanide, the mixture soon begins to turn blue, and after some days a considerable precipitate of the most beautiful prussian blue has formed. It is therefore evident that the æther or alcohol has either changed the percyanide into protocyanide or the persalt of iron into protosalt.

If ordinary sugar be added to the solution of percyanide, and the liquid be kept boiling for a few minutes, it is turned blue on mixing pernitrate of iron with it. The mixture will also appear blue if some of the salt of iron is added to it; after some hours, without any exposure to heat, and after some days there will be a considerable deposit of prussian-blue.

When the solution of percyanide is mixed and warmed with formic acid, it becomes blue without requiring any persalt of iron; if the mixture be evaporated until all acid is expelled and the residue extracted with water, this extract will afford with solution of nitrate of iron a precipitate of prussian blue. The same reaction takes place in the cold, only more slowly. Acetic, tartaric and citric acids, act in a similar manner on the solution of cyanide, and probably several other organic acids. Oxalic acid appears to have no action either at the ordinary or at an increased temperature. Uric acid is remarkable, above all other organic compounds, from its quick action on this salt. If it has stood for only a minute with a solution of percyanide, this is rendered blue on the addition of nitrate of iron. A solution of creosote in water has perhaps a stronger action; on shaking it for a few instants with a solution of percyanide, and then adding a persalt of iron, it is rendered strongly blue. If the excess of creosote has been expelled from the solution by heat, nitrate of iron causes a very considerable precipitate of prussian blue.

Cinchonine and morphine behave similar to uric acid and creosote, while strychnine and quinine appear to have no action.

When urea is conveyed into a solution of the percyanide, it appears to have no action, but on evaporating the mixture to dryness, and warming the residue so as to disengage ammonia, the mass becomes strongly blue. No change of colour ensues previous to the disengagement of ammonia.

The behaviour of nitrate of ammonia to the cyanide is likewise remarkable; if some of the salt be heated to fusion, and a few cry-

stals of the ferridcyanide of potassium conveyed into the liquid mass, it immediately becomes of a dark blue, and there is a strong smell of prussic acid. If the mixture is still further heated, it assumes a reddish-yellow colour, and now affords no further precipitate either with a persalt or protosalt of iron; but if the mass, while still blue, is treated with water, the filtered solution gives prussian blue with nitrate of iron. If a solution of the percyanide is added to one of neutral sulphate of ammonia, and the whole is evaporated to a pasty mass, it appears green. If it be now heated to fusion, it acquires a light blue colour, and if some water be poured over the mass thus treated, it becomes deep blue, and there is a separation of prussian blue. The filtered liquid is not rendered perceptibly blue by nitrate of iron.

If a few drops of hyponitric acid are added to a mixture of ferridcyanide of potassium and nitrate of iron, there is a precipitate of prussian blue. Since pure nitric acid produces no change in the above mixture, this reaction may be employed to detect even small quantities of nitrous acid in nitric acid. Nitric oxide has a very energetic action on a mixture of percyanide and nitrate of iron; each bubble of this gas, on entering the solution, becomes surrounded with a blue coating, and prussian blue is very rapidly thrown down. Nitrous oxide behaves with perfect indifference towards such a mixture.

Sulphurous acid likewise possesses in a high degree the power of altering the dissolved percyanide in such a manner that it shall afford blue precipitates with persalts of iron.

Since the precipitation of prussian blue by the nitrous acid, nitric oxide and sulphurous acid from a solution of the above-mentioned mixture of salts, might probably depend solely on those three combinations converting the persalt into protosalt, while they leave unaltered the percyanide, the author convinced himself that the three bodies mentioned also exercise a decomposing action on the solution of the percyanide.

It was to be supposed that the bodies which reduced the ferridcyanide of potassium to ferrocyanide would likewise have a reducing action on the persalts of iron; the following experiments entirely confirm this supposition. For instance, if a solution of nitrate of iron be left only for a few minutes, or for a shorter time, in contact with arsenic, antimony, bismuth, cadmium, lead, iron, zinc and tin, the solution of percyanide becomes perceptibly blue. Even copper, mercury and silver produce a similar change, but more slowly. Whether palladium, platinum and gold are able to effect it with time has not yet been ascertained.

Some protoxides, as for instance that of copper, when placed for a short time in contact with the solution of nitrate of iron at the ordinary temperature, alters the salt of iron in such a manner that the solution of percyanide is rendered blue by it.

Phosphorus appears to act more rapidly on the solution of the nitrate of iron than on that of the cyanide.

Sugar heated only for a short time with a solution of the persalt

of iron likewise causes it to give a precipitate of prussian blue in the solution of the cyanide. Formic acid, warmed but for a few instants with the dissolved salt of iron, induces the formation of so much protosalt, that on mixing this liquid with the percyanide prussian blue is precipitated. Citric, acetic and tartaric acids behave in a similar manner, but lithic acid is most remarkable from its deoxidizing action. If this acid be left in contact only for a minute with a solution of the nitrate of iron, the filtered liquid has acquired the property of precipitating prussian-blue from the solution of the percyanide. Warming of the solution hastens the reaction of the lithic acid.

Creosote even surpasses lithic acid by its deoxidizing action on persalts of iron. Cinchonine and morphine act in a similar manner, but not so rapidly. Nascent hydrogen, in contact with a solution of persalt of iron, imparts to it the property of precipitating prussian blue from the solution of the percyanide.

Nitrous acid, nitric oxide, sulphurous acid, and the combinations of hydrogen with selenium, phosphorus, arsenic, antimony and tellurium, behave in a similar manner.

Dilute solutions of oxalic acid, nitrate of iron and ferridcyanide of potassium were mixed and conveyed into a flask, into which nitric oxide, sulphuretted and phosphoretted hydrogen were introduced. According to the preceding statements these gases precipitate prussian blue from a liquid containing only nitrate of iron and percyanide; in the mixture however containing oxalic acid they cause no such precipitate, but in order to obtain this negative result it is requisite that there should not be too little oxalic acid present in the solution.

With respect to seleniuretted hydrogen, oxalic acid is not able to prevent entirely its action on the mixture, which immediately becomes blue. When a solution of the percyanide is placed in contact with lithic acid and oxalic acid, no blue colouring is produced by a persalt of iron, however long the substances may have been together, nor does heating in any way assist.

Oxalic acid likewise prevents sugar and other organic matters from altering the percyanide and the persalts of iron in the above manner, nor is there any prussian blue precipitated even on adding nitrous acid to a mixture containing percyanide, nitrate of iron and oxalic acid.

Besides the interest which these experiments offer, they likewise lead to ready methods of detecting nitric oxide, nitrous acid and sulphurous acid. Moreover, since the organic bodies employed in this reaction are likewise subject to decompositions, a more accurate investigation of these relations will probably lead to the knowledge of many new compounds.—*Journ. für Prakt. Chem.*, xxx. p. 129.

Further Researches on Ozone. By Prof. Schönbein.

M. Schönbein long since advanced the opinion, that the peculiar odour which accompanies the disengagement of oxygen at the posi-

tive electrode in the electrolyzation of water, is due to a peculiar substance analogous in a chemical point of view to iodine, bromine and chlorine. He has recently made some further researches on this subject, which appear to confirm this opinion, and lead him to believe that nitrogen itself is a chemical combination of ozone and hydrogen.

Independently of the electro-chemical process above mentioned, M. Schönbein has succeeded in liberating ozone by purely chemical processes. Thus it is disengaged when phosphorus is placed, at the ordinary temperature, in a mixture of nitrogen and oxygen, *i. e.* in atmospheric air. It is likewise disengaged when a mixture of peroxide of manganese, or of peroxide of lead, sulphuric acid and nitrogen, is exposed to heat. The manner in which ozone is produced, and a great number of other facts enumerated in detail in his memoir, lead the author to conclude that ozone is derived from nitrogen; in other terms, that nitrogen is a compound of ozone and hydrogen.

Nitric acid would appear to be ozonic acid; and in general the fact of nitrogen being a compound body would occasion considerable change in that portion of chemistry which relates to the nitrogen compounds.

M. Schönbein has obtained a body which he regards as very pure ozonide of potassium; it is a white powder, almost tasteless, scarcely soluble in water, easily decomposed by sulphuric acid, and liberating ozone without the presence of peroxide of manganese. It would appear that ozone forms compounds very different in their chemical nature from those produced by chlorine, bromine, &c. The compound of hydrogen and of ozone, and the ozonide of potassium, have very little resemblance to hydrochloric acid and chloride of potassium. With respect to its chemical affinity, the author has ascertained that it should be placed between bromine and iodine; ozone does not act on bromide of potassium, while it readily decomposes iodide of potassium.

It is not without importance to remark that, if nitrogen is really a compound body, this discovery will have considerable influence, not solely on several points of chemistry, but likewise on several branches of science, and especially on meteorology. The part taken by nitrogen in meteorological phænomena would become important, and the production of atmospheric electricity itself might be brought into connexion with the decomposition of that gas.—*Bibl. Univ. de Genève*, May 25, 1844.

On Urinary Calculi of the Chelonia. *By* M. Duvernay.

The urine of the Chelonia is a very watery, pale, limpid fluid. Several analyses, made first by Vauquelin, subsequently by MM. Lassaigne and Boissil, J. Davy, Stolze, J. Müller and Magnus, have shown that it contains uric acid, as also urea, but in small quantity. The only description of the urinary concretions of the Chelonia has been made by Vicq d'Azyr. He discovered a deposit in the urinary

bladder of a tortoise, which Vauquelin analysed, and found it composed of chloride of sodium, phosphate of lime, uric acid and animal matter. M. Lesueur has discovered that the *Trionix*, found in the river Wabash in the United States of America, and which he denominated *spiniferus*, was subject to the formation of vesical calculi. One of them, which I extracted from the bladder of a female, had an oblong form, was 0·017 millimetre long, 0·011 broad, and weighed 0·730 gr.; its surface was uneven, roughened by the slight projection of laminated processes, and as it were pitted with holes or pores. It was of a yellow colour, and had a specific gravity of 1·780 at 42° Fahr. When sawn through lengthwise, a small pearly lamina was perceptible, evidently a portion of a shell; this was yellowish-green on one surface, white and pearly on the other. The appearance and chemical properties of this lamina clearly showed its nature. The vesical calculus, when analysed, yielded in 100 parts as follows:—

Phosphate of lime	64·70
Carbonate of lime	15·10
Organic matters and water	20·20
	100·00

M. Lassaigne examined the proportion of lime to the phosphoric acid, by dissolving a certain quantity of it in water acidulated with the smallest possible quantity of muriatic acid, and precipitating the lime by oxalate of ammonia. The oxalate was subsequently calcined and transformed into anhydrous sulphate of lime, and thus the exact proportion of lime estimated. In two experiments, M. Lassaigne found—

Phosphoric acid	53·87
Lime	46·13
	100·00

The phosphate thus differed essentially from that of bones, and was more like Berzelius's neutral phosphate.

The second calculus was larger; it weighed 262 grs., was of a round, slightly flattened form, yellowish-white outside, white inside. It was composed of concentric layers; the most external contained fragments of shells. Its specific gravity was 1·875. On analysis it yielded—

Phosphate of lime	56·19
Carbonate of lime	3·04
Carbonate of magnesia	1·10
Silica, in transparent grains	4·76
Salts and soluble organic matters	1·91
Animal matter insoluble in water	13·00
Water	20·00
	100·00

M. Lesueur supposes that, in consequence of the peculiar mode of termination of the bladder in the cloaca, the débris of shells, which pass into the cloaca from the rectum with the excrements, or

which enter with the water, which is supposed to be forced in by the walls of the cloaca, are, in these rare cases, thrown back into the bladder, thus forming the nucleus of the concretion.—*Comptes Rendus*, July 30, 1844.

Investigations upon Decay and Mouldering of Wood. *By* M. Hermann.

Under the name of mould-rot (*Humusfaülniss*) the author distinguishes that kind of decay which takes place in wood when freely exposed to air and moisture, and which hitherto, in accordance with the views of Liebig, has been regarded as arising simply from the assimilation of oxygen and formation of 1 atom of carbonic acid and 2 atoms of water for every 2 atoms of oxygen absorbed. The changes however which wood undergoes in this kind of decomposition are not of so simple a character, but, upon the contrary, very complicated and difficult to unravel. It is easily proved that during the decomposition of wood, carbonic acid and water separate; but the volume of atmospheric air, so far from remaining unchanged during that process, becomes either increased or diminished according to the different stages through which the wood passes in the progress of decay. Moreover, the fact that, in the decomposition of wood, not merely oxygen, but also nitrogen is absorbed from the air, had hitherto been entirely overlooked; that ammonia results, and finally, that not only humic acid, but also humic or mould extract and nitroline are formed.

It has been already enounced by Hermann, that at the origin of the various substances arising from decay, nitrogen is absorbed from the atmosphere. Mülder, who likewise succeeded in detecting the presence of nitrogen in many of these substances, supposed it to be owing to the ammonia they had imbibed from the air; but in order to explain the circumstance that the ammonia contained in the humic acids could neither be removed by alkalies nor acids, he advanced the hypothesis, that the mould substances possessed so great an affinity for ammonia, that it was not possible to remove a certain portion of the latter by any means.

With a view of confirming his view of the subject, the author instituted the following experiments:—

The first had reference to the changes produced in the composition of the atmospheric air by the decomposition of wood. For this purpose he selected a piece of wood which had been cut in such a manner from another piece of wood beginning to rot, that the greatest part of the sample was in a fresh condition, the extreme outer portions only being decomposed.

28 cubic parts of this wood, in a moist state, were left in contact over mercury with 262 cubic measures of atmospheric air, and at a temperature of 74° Fahr., for the space of 10 days; at the expiration of which time the wood was removed. The air which remained contained a considerable quantity of carbonic acid, though its volume was precisely the same as before, 262 cubic

measures. Now if we consider that the wood had remained in contact with the air, and in a moistened condition, it is not to be denied that this moisture must have absorbed a certain quantity of carbonic acid which was removed with the wood. Hermann estimates the volume of this carbonic acid at 13 cubic measures. The remaining 262 measures of air resolved themselves upon analysis into 40 cubic measures of carbonic acid, 194 cubic measures of nitrogen and 28 of oxygen.

Now since the 262 cubic measures of atmospheric air originally employed consisted of 207 nitrogen and 55 c. m. of oxygen gas, but after contact for 8 days with 28 c. m. of decaying wood there were only 194 of nitrogen and 28 of oxygen left, it follows that $207 - 194 = 13$ c. m. nitrogen, and $55 - 28 = 27$ c. m. oxygen, were assimilated by the decomposing wood, and were replaced by 40 c. m. of carbonic acid + those 13 c. m. (*i. e.* 53 c. m. carbonic acid) which had been removed with the moisture of the wood.

In the decay of fresh wood, therefore,

1 c. m. of nitrogen and
2·0 c. m. of oxygen gas

are absorbed from the air, and replaced by 4 c. m. of carbon.

The second experiment was made to determine the changes which *decomposed* wood induced in atmospheric air. When wood in a state of complete rottenness, but which still contains nitroline, is brought into contact with atmospheric air, the following results are obtained:—

21 c. m. of rotten wood were submitted to 186·3 c. m. atmospheric air, for the period of 5 days, at a temperature of 67° Fahr. At the end of this time the volume of the air left amounted only to 182 c. m., which consisted of—

Nitrogen	143·7	cubic measures.
Oxygen	11·3	...
Carbonic acid gas	27·0	...
	182·0	...

The 186·3 c. m. atmospheric air consisted, on the contrary, of—

Nitrogen gas	147·2	cubic measures.
Oxygen	39·1	...
	186·3	...

Consequently $147·2 - 143·7 = 3·5$ of nitrogen, and $39·1 - 11·3 = 27·8$ of oxygen were assimilated by the rotten wood, and replaced by 27·0 carbonic acid.

That ammonia is formed during the decomposition of wood, is concluded from the circumstance that all rotten wood, and many kinds of turf which he has had an opportunity of testing, have been found by him to contain ammonia. It is easy to be convinced of the presence of ammonia in these substances by moistening them with caustic potash, and then holding a glass rod immersed in hydrochloric acid over it. The usual white vapours of sal-ammoniac then make their appearance. Spring waters which have passed

through turf or strata of soil containing decomposed vegetable substances usually contain ammonia.

Now, since it has been proved that wood during its decomposition absorbs nitrogen from the atmosphere, and thus becomes converted into nitroline, we are justified in admitting that ammonia is produced during further progress of decomposition from nitroline, in a manner precisely similar to its formation during the putrefaction of any other nitrogenous organic substance. From the important office which ammonia fills in vegetation, it has been wisely ordained in the œconomy of nature that it should be abundantly produced in situations where it is so necessary to the maintenance and wants of vegetable life, and through this of animal existence likewise. On this account has nature associated the formation of humus with the production of ammonia.

The quantity of ammonia contained in rotten wood and turf varies considerably according to the degree to which the formation of soil has advanced, or whether the ammonia has become exchanged for other bases contained in the water that comes in contact with the mould substances. The maximum of ammonia found by Hermann in rotten wood amounted to 1 per cent. of its weight.

Hitherto it had been the received opinion that rotten wood contained only humic acid; but the author has already proved, by experiments upon mould, that three distinct organic substances occur in it—nitroline, ligneo-humic acid, and humus or mould extract.

Hermann has since found another kind of nitroline, which contains much less nitrogen, and is of more frequent occurrence. Its composition is as follows:—

	Found.	Equiv.		Calculated.
Carbon	57·1	32	= 2422·4	57·01
Hydrogen	6·0	18	249·6	5·87
Nitrogen	4·0	1	177·0	4·16
Oxygen	32·9	14	1400·0	32·96
	100·0		4249·0	100·00

Fresh decomposed wood was found by Hermann to be composed of—

Nitroline	61·0
Ligneo-humic acid	21·0
Humous extractive	17·5
Ammonia	0·5
	100·0

Decayed wood, in which the formation of humus was further advanced, consisted of—

Nitroline	18·875
Ligneo-humic acid	53·625
Humous extractive	26·500
Ammonia	1·000
	100·000

Hermann concludes from these facts, that two entirely different processes require to be distinguished during the decomposition of wood, the formation of nitroline and that of humus, the latter succeeding the former, and humus thus including all the parts of rotten wood soluble in alkalies. That from 1 atom of wood = $C^{36} H^{22} O^{22}$ (according to Liebig) 4 atoms water, 4 atoms carbonic acid and 1 atom nitroline can originate by the absorption of 4O and 1N is perfectly evident; but from this nitroline very distinct kinds of wood-humus can originate, as exhibited by the analysis of decayed wood communicated above. The woody humus of the first analysis corresponds, supposing 9208·6 to be the atomic weight of ligneo-humic acid and 4221·4 that of humous extract, to a combination of 1 atom ligneo-humic acid, 2 atoms humous extract, and 1 atom ammonia; the second woody humous contains equal atoms of all three substances. In the first case it would require 5, in the second 4 atoms of nitroline, with the absorption respectively of 58 and 56 O and $1\frac{1}{2}$ N to furnish these results. In an experiment however the absorption of nitrogen was found to be twice as great as required; it is therefore probable that far more ammonia is formed in this decomposition of the nitroline, perhaps 3 atoms, 2 of which escape, and only 1 remains with the woody humus. In the first case then there would be formed from 5 atoms nitroline, 52 O and $3\frac{1}{2}$ N 1 atom ligneo-humic acid ($C^{70} H^{35} O^{23} N^{3\frac{1}{2}}$), 2 atoms humous extract ($C^{32} H^{16} O^{14} N^2$), 3 atoms ammonia, 26 carbonic acid and 14 water; in the second case, from 4 nitroline, 50 O and $3\frac{1}{2}$ N, 1 ligneo-humic acid, 1 humous extract, 3 ammonia, 26 carbonic acid and 12 water.—*Journ. für Prakt. Chem.*, xxvii. s. 165.

PHARMACOLOGY.

On the Febrifuge Properties of Variolaria amara. *By* Dr. Dassier.

This lichen grows in the form of large grayish crusts upon the bark of beech-trees in mountainous regions. When reduced to powder, it excites its influence upon the pituitary membrane, and applied to the tongue, very speedily gives rise to a distinct bitter taste, which increases by degrees, and is retained for a considerable length of time. It was examined in 1831 by M. Alms, who extracted from it a bitter principle, to which he gave the name of *picrolichenine*. If taken into the stomach, the powder of *Variolaria* creates an appetite, and acts like all bitter tonics by rousing the digestive powers and imparting a new vigour to the constitution. It does not appear to exercise any influence upon the nervous system, like sulphate of quinine. By reason of its excessive acerbity, the *Variolaria* cannot be prescribed in the form of a moistened powder in a vehicle such as quina. M. Dassier has administered it in the shape of pills incorporated with conserve of roses, or in that of lozenges mixed with chocolate. It is best to prescribe it in doses of 7 to 15 grs.

for adults, to be taken in the course of 24 hours, and of 3 to 6 grs. for children under 10 years of age. In quotidian and tertian fevers, those in which the *Variolaria* has proved itself most efficacious, it has acted beneficially after the first or second dose, and 7 to 9 grs. have very often been sufficient to effect a cure. In cases however where the first doses do not act, we cannot reckon upon any good results.

M. Dassier has given *Variolaria* in a very great number of intermittent, quotidian, tertian and quartan fevers. In the second of these he has almost constantly, in the third kind frequently, in the last rarely obtained a cure. It is true that he has never exceeded the dose of 1 grm. in the course of 24 hours. Despite the encouraging observations of M. Dassier, we are of opinion that the *Variolaria* should only be prescribed under the following circumstances:—

1. As a substitute for sulphate of quinine.
2. In cases of mild quotidian or tertian fevers.
3. That recourse should never be had to its use where we suspect a severe attack of fever, or one that may assume a dangerous character.

It would be interesting, on account of its low price and the ease with which it can be procured, to ascertain whether, if given in larger doses than has been above specified, its properties might not prove more efficacious. At all events, new researches upon the active principle of this lichen are well deserving of being made.—*Journ. de Pharm.* for July 1844.

CHEMICAL PREPARATIONS.

Preparation of Narcotic Extracts. By Scheidemandel.

The author describes his method, which he particularly recommends for the preparation of these extracts in small quantities, as follows:—

In this neighbourhood (Creussen) Hyoscyamus, Belladonna, Digitalis, Conium, &c. grow wild. I therefore gather the plants at the proper time, dry them carefully, and use them in the preparation of the extracts in the following manner:—

The plant, Hyoscyamus for instance, is thoroughly dried in a stove by a very gentle heat, until capable of being rubbed through a coarse horse-hair sieve. The very finest powder is separated and rejected.

The coarse powder thus obtained I place in a glass funnel of a certain capacity, the neck of which is partially obstructed by cotton loosely thrust into it, and on the top a piece of white filtering paper covered with a layer of sand, which has previously been purified with hydrochloric acid and well washed; this I also well wash after each operation, and dry and preserve for further use. The funnel holds exactly 4 oz. of coarsely-powdered Hyoscyamus. When it is

thus arranged, I gradually pour on it spirits of wine of spec. grav. 0·950, in such proportion that the powder is penetrated by it to half the depth of the funnel. I now desist, and find in about half an hour the spirit has penetrated the powder throughout the whole depth of the funnel, and an alcoholic extract of a dark green colour begins to drop into a glass vessel placed beneath.

When the dropping begins to slacken, I commence adding small portions of spirits of wine, about ½ an oz. every quarter of an hour. If I commence the operation at 9 A.M., I can progress so far that by the evening I have added the last portion of the spirit, using 18 oz. of spirit in all. I now cover the funnel with a glass plate, and commence the next morning adding pure water in successive small quantities of an ounce in the same manner as with the spirit. This is continued until the drops are no longer green but brown, that is, until all the alcoholic extract is displaced by the water, and the watery extract begins to fall from the funnel. When this takes place, the receiver containing the spirituous extract is removed and well covered, and replaced by an empty one. The alcoholic solution in the glass removed is of a remarkably fine green colour, with the well-known repulsive odour of Hyoscyamus. The treatment with the water is persevered in during the day in the same manner as with the alcohol, until the dropping fluid becomes transparent; I now once more add water; it is then covered with the glass plate, and allowed to drain quietly during the night.

Whilst this extraction with water is going on, I filter the alcoholic solution from the waxy matter, and distil off the alcohol in a small steam apparatus, until only a few ounces remain. The fine green syrupy residue I then pour into a porcelain dish, and add to it the watery solution when evaporated to a syrupy consistence, and evaporate it gently over the flame of a small spirit-lamp until of the proper consistence, by which means I procure an extract that dissolves completely in water with a fine green colour, and in point of activity leaves nothing to be desired. I proceed in the same manner with Belladonna, Digitalis, Conium, &c., and especially recommend this method to pharmaceutists in small places, as affording a certain and active product both in a quantitative and qualitative respect.

I have always obtained 1 oz. 6 drms. of extract from 4 oz. of coarsely-powdered Hyoscyamus.—Buch. *Rep.* xxxiii. pp. 58–61.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Source and Nature of Colouring Substances of Organic Origin, and on the Action of Oxygen upon them. *By* F. PREISSER.

[Continued from p. 415.]

Bixine.

ANNOTTO is a tinctorial substance, respecting the chemical constitution of which very little is yet known. John analysed the pulp

which surrounds the seeds of the *Bixa orellana*, and which had not undergone fermentation; but this analysis gives very little information respecting the colouring principle*. M. Boussingault has described the principal chemical properties of the commercial annotto, without however examining the substances to which it owes its tinctorial properties†. M. Chevreul has endeavoured to elucidate this point. According to him, annotto contains two distinct colouring principles, viz.—

1. A yellow principle, soluble in water, alcohol, and sparingly in æther. It fixes well on alumned silk and wool, which it dyes yellow.

2. A red principle in the dry state, sparingly soluble in water, but soluble in alcohol and æther, which it colours orange red. It is characterized by the property of becoming indigo-blue by contact with concentrated sulphuric acid.

The best prepared annotto contains proportionally more of the yellow principle than the ordinary kind; M. Chevreul does not however mention the method which he used to separate the two colouring matters, nor whether he obtained them in a pure state‡.

We have made the following experiments on annotto:—The interior yellowish-red portion of a piece of excellent annotto was treated with a very weak solution of carbonate of soda; the brownish-red solution precipitated by hydrated oxide of lead, which entirely separated the colouring matter. The lake was decomposed by sulphuretted hydrogen; and the liquors, rapidly filtered and evaporated, afforded small white acicular crystals, which lined the sides of the vessel. It is to this crystalline substance that we have given the name of *bixine*, derived from *Bixa orellana*, the tree which produces the annotto.

Bixine is of a pale yellowish-white colour, and possesses a rather disagreeable bitter taste. It is very little coloured by contact with air; by length of time however it acquires a yellow tint, without any mixture of red. Under water it preserves its whiteness. It is volatile, soluble in water, but much more so in alcohol and æther. Sulphuric acid colours it yellow and dissolves it, without producing with it the blue tint which occurs with commercial annotto. Nitric acid turns it perceptibly yellow. Chromic acid and the bichromate of potash act slowly upon it; it assumes under their influence an orange-yellow tint, and crystallizes of this colour.

The beautiful dark red colour of annotto is due to the simultaneous action of the air and of ammonia on bixine, which is converted by them into a new substance, *bixeine*.

It was found quite impossible to obtain *bixeine* in crystals; it forms a dark brown-red powder, and in this state becomes blue by contact with sulphuric acid. This substance has weak acid properties; it combines readily with alkalies and oxide of lead. It pos-

* John, "Annales de Chimie," t. lxxxviii. p. 99.

† Boussingault, "Sur les Propriétés Chimiques du Roucou."—*Ann. de Chimie et Physique*, t. xxviii. p. 440.

‡ Chevreul, "Leçons de Chimie appliquée à la Teinture," t. ii. 38e leçon, p. 183.

sesses moreover the chemical characters of annotto. This matter deserves further investigation.

In order to impart to the annotto a brilliant red colour, it is mixed from time to time with urine. This probably converts the *bixine* into *bixeine*?, which is the more likely, since the interior of the lumps of annotto is yellow, and the red colour is only external where the air can have access to it.

Rhamnine.

The berries of the different species of *Rhamnus* are very much used for dyeing, under the names of *Spanish*, *Turkey* and *Persian* berries. According to M. Chevreul, they yield to water, amongst other bodies—

1. A yellow colouring principle, which is united with a substance insoluble in æther, sparingly soluble in concentrated alcohol, and very soluble in water. It appears to be very volatile.
2. A matter remarkable from its intense bitterness, and which is soluble in water and in alcohol.
3. A red principle, which exists only in small quantity, and which decomposes into a brown substance under the influence of air. It is principally found in the residue of the aqueous extract of the berries, and is insoluble in æther and alcohol*.

Persian berries of excellent quality were bruised in a mortar, and then treated with æther, which acquired an olive-yellow colour. The liquor was evaporated in a retort to two-thirds, and the residue mixed with water, which became of a dark yellow colour. Some hydrate of lead, added in small quantity, precipitated a brown-yellow lake; fresh hydrate added to the filtered liquid then gave a beautiful lake of a very vivid yellow. This last was decomposed by sulphuretted hydrogen. The filtered liquor was scarcely coloured yellow; but notwithstanding every attempt to obtain well-characterized crystals, it only gave a crystalline powder of a slightly yellowish white, which was nearly deprived altogether of colour by washing in æther and pressure between folds of paper. To this substance we apply the name of *rhamnine*.

The crystalline powder has great analogy with *quercitrine* obtained when disturbed during crystallization. It has a bitter taste, is soluble in water, in alcohol and æther. Exposed to the air, the solution rapidly becomes yellow. Acids turn it yellow, alkalies immediately dark brown; barytes and lime-water produce the same effect.

Rhamnine, under the influence of oxidizing agents, such as nitric and chromic acids, bichromate of potash, sulphuric acid and peroxide of manganese and free oxygen, becomes of a dark yellow colour, and is converted into a new principle, which we name *rhamneine*.

Rhamneine may be obtained by exposing a solution of rhamnine to the atmosphere; it crystallizes with great difficulty, and forms a

* Chevreul, "Leçons de Chimie appliquée à la Teinture," t. ii. 30e leçon, p. 174.

dark yellow powder, which appears under the microscope to consist of minute crystals.

This substance behaves like a true acid towards litmus and bases. With oxide of lead, lime and alumina, &c., it forms orange-yellow salts, *rhamneates*, in definite proportions.

Rhamneine is not very permanent when in the free state. By contact with the air or pure oxygen, it absorbs this element in the course of time, and becomes of a red and brown colour, to which the red and brown matters always present in decoction of Persian berries owe their origin.

Fustine.

As yet we possess no good analysis of the wood of fustic (*Rhus cotinus*). We only know that it contains a yellow, a red and a brown colouring matter, and an astringent principle. According to M. Chevreul, the colouring matter appears capable of crystallizing. It is generally in the form of a brilliant varnish, of a slightly orange-yellow colour approaching to green*.

To obtain the colouring principle of the fustic in a state of purity, we began by separating the tannine from the decoction with a little gelatine; then evaporated the liquid, which when filtered was of an olive-yellow colour, nearly to dryness, and the residue was redissolved in æther. The coloured solution was again evaporated in a retort, water added to it, and precipitated by hydrated oxide of lead. The yellow lake was decomposed by sulphuretted hydrogen. A colourless liquid was obtained, which deposited some small colourless crystals; they were completely and easily purified by washing with æther. We give the name of *fustine* to this crystalline principle.

The taste of *fustine* is slightly bitter. It is soluble in water, alcohol and æther. The solutions in contact with the air become somewhat rapidly coloured at the edge of the vessels. Sulphuric acid dissolves it, giving it a bright yellow tint. Nitric acid colours it more rapidly, especially on the application of a gentle heat. Persulphate of iron turns it to a dark olive green. Acetate of lead precipitates it white, but the precipitate becomes gradually yellow. Potash, soda and ammonia immediately give it a beautiful red colour.

Fustine has a very great tendency to absorb oxygen, being converted into *fusteine*. In other respects it possesses a strong analogy with rhamnine.

Chlorophylle.

Notwithstanding the researches of Pelletier and Caventou†, of Macaire Princep‡, Berzelius§ and Pelletier‖, but very little is known

* Chevreul, "Leçons de Chimie appliquée à la Teinture," t. ii. 32e leçon, p. 169.

† "Notice sur la Matière Verte des Feuilles."—*Journ. de Pharm.*, t. iii. p. 486, 1817.

‡ "Mémoire sur la Coloration Autumnale des Feuilles."—*Ann. de Chim. et Phys.*, t. xxxviii. p. 515, 1828.

§ Traité de Chimie, t. v. p. 324, and t. vi. p. 41. Journ. de Pharm., t. xxiii. p. 333 and 939. Traité de Chimie Organique de Liebig, t. ii. p. 430.

‖ Ann. de Chim. et de Phys., t. li. p. 195.

respecting the green colouring matter of leaves, which undergoes such remarkable changes of colour on the approach of cold, especially in some plants whose foliage becomes bright red or of a beautiful lemon-yellow. It is very probable that the modifications of colour presented by chlorophylle depend, as Macaire Princep has advanced, on the fixation of oxygen; but this subject requires further examination.

Up to the present time we have made but few experiments on the green matter of leaves. We will here mention only one of our results, which supports what we have advanced relative to the action of oxygen on the colouring principles.

Some green leaves were crushed in a porcelain mortar. The green liquor which resulted from it was treated, after filtration, with a little hydrate of lead, which entirely precipitated the green matter and discoloured the liquor. The lake was decomposed by sulphuretted hydrogen. The filtered liquid was without colour. It was passed under a bell-glass full of mercury containing oxygen. After a few days a portion of the gas was absorbed, the liquid was coloured green, and had deposited some flakes of a darker green. The absorption of the gas had taken place more especially under the influence of the solar light.

On evaporating to dryness the yellowish liquid, obtained by decomposing the lead salt by sulphuretted hydrogen, we obtained a matter having much analogy with the *xanthophylle* of Berzelius.

We propose returning to this subject, which deserves very careful investigation.

Mode of colouring Daguerreotype Pictures. By CHARLES G. PAGE, M.D., Prof. Chem., Columbia College, Washington, D. C.

In the month of December 1842, I instituted a course of experiments to determine the effects of oxidation upon the surface of Daguerreotype pictures, and arrived at some beautiful results in fixing, strengthening and colouring these impressions. Numerous and arduous duties of a public nature have prevented me from investigating the subject as I wished, and I therefore present the facts, for others to adopt, as the basis of what promises to be a most interesting course of study and experiment.

First, a mode of fixing and strengthening pictures by oxidation :—

The impression being obtained upon a highly polished plate, and made to receive by galvanic agency a very slight deposit of copper from the cupreous cyanide of potash (the deposit of copper being just enough to change the colour of the plate in the slightest degree), is washed very carefully with distilled water, and then heated over a spirit-lamp until the light parts assume a pearly transparent appearance. The whitening and cleaning up of the picture by this process is far more beautiful than by the ordinary method of fixation by a deposit of gold. A small portrait fixed in this way, more than a year since, remains unchanged, and continues to be the admiration of persons interested in this art. One remarkable effect produced

by this mode of fixing is the great hardening of the surface, so that the impression is effaced with great difficulty. I have kept a small portrait, thus treated, unsealed and uncovered for over a year, and have frequently exposed it in various ways, and rubbed it smartly with a tuft of cotton, without apparently injuring it; in fact, the oxidized surface is as little liable to change as the surface of gold, and is much harder. As copper assumes various colours, according to the depth of oxidation upon its surface, it follows that if a thicker coating than the first mentioned can be put upon the plate without impairing the impression, various colours may be obtained during the fixation. It is impossible for me to give any definite rules concerning this last process, but I will state, in a general way, that my best results were obtained by giving the plate such a coating of copper as to change the tone of the picture, that is, give it a coppery colour, and then heating it over a spirit-lamp until it assumes the colour desired. I have now an exposed picture treated in this way at the same time with the two above mentioned, and it remains unchanged. It is of a beautiful green colour, and the impression has not suffered in the least by the oxidation. Should this process be perfected, so as to render it generally available, it will be greatly superior to the present inartistical mode of stippling dry colours upon the impression; for the colour here is due to the surface of the picture itself. For pure landscapes it has a pleasing effect, and by adopting some of the recent inventions for stopping out the deposit of copper, the green colour may be had wherever desired. In some pictures a curious variety of colours is obtained, owing to the varying thickness of the deposit of copper, which is governed by the thickness of the deposit of mercury forming the picture. In one instance a clear and beautiful ruby colour was produced, limited in a well-defined manner to the drapery, while all other parts were green. To succeed well in the first process, viz. that for fixation and the production of the pearly appearance, the impression should be carried as far as possible without solarization, the solution of the hyposulphite of soda should be pure and free from the traces of sulphur*, the plate should be carefully washed with distilled water, both before and after it receives the deposit of copper; in fact, the whole experiment should be neatly performed, to prevent what the French significantly call *taches* upon the plate when the copper comes to be oxidized.—*Journ. of Franklin Inst.* for May 1844.

* The presence and deposit of sulphur is a fault of most of the hyposulphite of soda of commerce, and it is the action of this sulphur upon the silver that puzzles so many Daguerreotypers, by clouding, staining and marking the plates in various ways. It may be obviated by repeatedly filtering the solution, or by keeping it in lightly corked bottles a long time before it is used.

In addition to the above, I may state that exposure of the coppered picture to the vapour of hydrosulphuret of ammonia produces sometimes a pleasing effect, but usually spoils the impression.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

May 20, 1844. (T. Graham, Esq., Vice-President, in the Chair). The following communications were read:—

"On the Composition of Narcotine, and some of the Products of its Decomposition by the Action of Bichloride of Platinum," by J. Blyth, M.D.

The equivalent of narcotine, determined by Liebig by saturating the alkaloid with dry hydrochloric acid gas, is 4799; this, combined with the results of its analysis, led to the formula $C^{40}\,H^{20}\,N\,O^{12}$. M. Regnault obtained, by this method of operating, the numbers 5139, 5127·6 and 5253, and deduced from his analyses the formula $C^{44}\,H^{23}\,N\,O^{13}$. More recently M. Liebig has attempted a solution of the question by examining the double salt formed by bichloride of platinum and narcotine, but the results differ very considerably from those of the former method. At the suggestion of M. Liebig, Mr. Blyth was induced to undertake a re-examination of the equivalent of narcotine, of which the present paper is a summary.

It appears that, in the method adopted, two distinct sources of error exist,—1st, the double platinum salt is decomposed by long-continued washing; and 2nd, by the reaction of the excess of bichloride of platinum upon the compound at a temperature even much below 100°. In such cases the supernatant liquid acquired an orange colour, and deposited on cooling large dark red crystals mixed with white needles, which on examination proved to be opianic acid, a substance recently obtained by Liebig and Wöhler by the action of sulphuric acid and oxide of manganese upon narcotine.

Precautions being taken to avoid both these errors, the equivalent of narcotine, as deduced from the analysis of the double salt, was found to be represented by the numbers 5235. This agrees very well with the formula $C^{46}\,H^{25}\,NO^{14}$.

The red crystallized salt obtained by heating the double chloride of platinum and narcotine with excess of chloride of platinum, was not examined. Its production is accompanied by that of opianic acid, and of a substance much more soluble than opianic acid, which separates in rhombic prismatic crystals. The red salt is termed by Dr. Blyth, "Platinchloride of Cotarnin." It forms large red six-sided prisms, slightly soluble in hot water, and not decomposed by that liquid even at a boiling temperature. It consists of $C^{25}\,H^{14}\,N\,O^{6}\,Pt\,Cl^{3}$.

Cotarnin itself, separated from this compound by means described in the paper, is a colourless substance which crystallizes in needles grouped in stars. It is soluble in water, and has the properties of a base. It is composed of $C^{25}\,H^{13}\,N\,O^{6}$.

The composition of opianic acid was found by the author to be represented by the formula $C^{20}\,H^{9}\,O^{10}$, which agrees with the experiments of Wöhler.

Hemipinic Acid.—This is the substance mentioned above as separating from the mother-liquor of the red salt and opianic acid. The crystals effloresce on exposure to the air, and are very soluble in water. Its reactions are quite different from those of opianic acid. Hemipinic acid contains $C^{10} H^4 O^5$.

Another body, narcogenine, intermediate between narcotine and cotarnin, is sometimes produced in these changes, although the exact circumstances under which it appears are not exactly known.

"On the Inorganic Constituents of Plants," by Drs. H. Will and Fresenius.

After alluding to the value and importance of a correct knowledge of the inorganic constituents of plants as an object of high interest in agriculture and vegetable physiology, and cursorily reviewing the labours of De Saussure, Berthier and others, on ash analyses, the authors proceed to detail the methods of examination which they have, by a long series of experiments, found to be best fitted for the purpose, detailing at length the precautions which are necessary to be attended to in these investigations, and classing the analytical processes according to the preponderance of certain ingredients. A great number of ash analyses, many of them conducted under the superintendence of Dr. Will, are then arranged in a tabular form, as of tobacco from various districts in Hungary; red and white wheat, the seed and straw of rye, peas, the wood of the apple tree, also mistletoe and lichens growing on the same, from the neighbourhood of Giessen. And these are followed by other tables of analyses, many of them comparative, by various experimenters. These are classed under two principal heads, namely, 1st, seed ashes, containing tribasic phosphates, sometimes also mixed with bibasic, as peas, beans, Coniferæ, and the *Brassica Napus*; and 2nd, those containing bibasic phosphates, as wheat, rye, buckwheat, maize, barley, millet, hempseed, linseed and oats. Analyses of saintfoin, the acorn, and the horse-chestnut are also appended.

PATENT.

Patent granted to Arthur Wall, Poplar, Middlesex, *for certain Improvements in the Manufacture of Iron.*

The first part of this invention consists in adding to the iron, while in a state of fusion in the smelting, puddling, balling or reheating furnaces, certain compound masses, which the patentee has designated, for more clearly explaining his process, A and B.

The composition A is a mixture of steel or wrought iron, in a comminuted state, such as filings or fine cuttings, with melted rosin, in the proportion of 2 lbs. of filings to 5 lbs. of rosin; it is made into balls of 5 lbs. each, and thrown upon the melted iron, in the ratio of 1 ball to 5 cwt. of metal. If preferred, instead of the

rosin, other resinous substances, and the varieties of turpentine, asphaltum, tar and pitch may be substituted; and a few pounds of charcoal may be added to the composition. The composition B is a mixture of common salt, rosin and charcoal, or other carbonaceous matter, which is made into balls, and thrown upon the fused iron, after it has been acted upon by the balls A in the proportion of 1 lb. of the composition B to each hundred weight of metal. Certain other fluxes, such as borax, nitre or fixed alkalies, may be substituted for the salt.

The second part of this invention consists in subjecting the iron, while in a fluid state, and while in the act of solidifying, to a current of electricity, which is caused to traverse the whole mass.

In casting a bar or similar mass, the electric current is caused to pass from end to end, by conductors so arranged that when the metal runs into the mould it may complete the electric circuit, or by means of a wire or wires passed from one end of the mould to the other. If the castings are horizontal, a piece of wrought iron, or other conducting material, is placed at each end of the mould, which is made of sand, or other non-conducting substance. These conductors are then connected by wires with a galvanic apparatus, or voltaic pile, or electro-magnetic or other battery; so that, when the melted iron is run into the mould, it will complete the electric circuit; and the patentee prefers to continue the electric current for some time after the iron has solidified. When the castings are vertical, a similar arrangement is made for the passage of the electric current through the metal, by placing a conductor at the top and bottom of the mould, in such a manner that the electric circuit will be completed the moment the mould is filled with the liquid iron.

To apply electricity to iron in a smelting furnace or cupola, a wrought iron rod is introduced through or at the side of the tap-hole, until it comes in contact with the melting metal, and another wrought iron rod is introduced at the upper and posterior part of the hearth, or through one of the tuyère holes, until it reaches the metal; the outer ends of these rods being then connected with a battery, the electric current will be caused to pass through the iron, care being taken not to continue it so long as to entirely decarburate the iron and bring it to a malleable state. When the electricity is to be applied to the iron in a puddling or balling furnace, two iron rods are also used, one of which is inserted into the fused metal, and the other end is connected with a battery; the other rod is attached to an insulating handle of porcelain, pottery, or other non-conducting substance, and a wire from the battery is connected to it close to the handle. By means of the handle, the extremity of the rod is caused to traverse the iron in its melted state or during its transition to the solid state, and the electric current will therefore pass through the metal in every possible direction.—Sealed Nov. 18, 1843.

THE CHEMICAL GAZETTE.

No. XLVIII.—October 15, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the various Modifications of Titanic Acid. *By* H. Rose.

When titanic acid is dissolved in a strong acid, such as sulphurci or hydrochloric acid, it is completely precipitated from the solution diluted with water by ammonia; and when washed until the water shows no trace of the acid in which the titanic acid was dissolved, the latter is also free from it.

The titanic acid, precipitated by ammonia, is perfectly soluble in acids, both while moist and when dried, and the solution may be diluted with cold water without becoming troubled. It is absolutely necessary however to its perfect solubility that it be washed with cold water, and no increase of temperature be employed in drying it; it must therefore be thoroughly dried over sulphuric acid. If these precautions be not observed, the solution in hydrochloric acid will not be clear, and will appear, on dilution with water, more or less opalescent. By the edulcoration of the titanic acid, precipitated by ammonia, with hot water, or by increasing the temperature during the drying, a portion of the titanic acid is modified, and is no longer soluble in acids.

By treating the anhydrous fluid chloride of titanium with water, a very perceptible increase of temperature takes place, and the solution is therefore not clear, but cloudy; but if, on the other hand, the chloride of titanium be dissolved in water so very gradually that all elevation of temperature is avoided, a clear solution is obtained. If the titanic acid precipitated by ammonia has been dried over sulphuric acid *in vacuo*, it is a hydrated acid; but besides water it contains ammonia, although in extremely small quantity, and which is not got rid of by the most careful washing with cold water. On heating the perfectly washed hydrated titanic acid to redness, the ammonia and water are expelled together. The author found in one experiment 1·62 per cent. of NH^3. It is difficult to determine the proportion of water contained in the hydrated acid. The titanic acid precipitated by ammonia was dried over sulphuric acid until it ceased to lose weight, which required a considerable time; it experienced a further loss of weight when placed over sulphuric acid *in vacuo*. The quantity of water obtained by Rose on heating the hy-

drate was variable; he found 11·35, 12·41, 12·67, and 12·81 per cent., and without the air-pump 15·00, 18·52, and 16·37 per cent. From this quantity obtained by heat, however, 2·47 per cent. of hydrated ammonia (corresponding to 1·62 dry ammonia) must be deducted; so that the hydrated titanic acid consists in 100 parts of—

Hydrate of ammonia	2·47
Water	9·84
Titanic acid	87·69
	100·00

The water contains 8·75 parts, the titanic acid 34·82 parts of oxygen; the latter therefore 4 times as much oxygen as the water.

When hydrated titanic acid is heated out of contact of the air, it becomes blackish, which may be attributed probably to a partial reduction effected by the ammonia. Heated to redness in the air, the hydrate becomes brown, and the fragments exhibit a pretty strong lustre.

The titanic acid precipitated by ammonia becomes incandescent by heating to redness, like oxide of chrome. It becomes weaker in proportion as the precipitated acid has been washed with hot water.

This incandescence takes place even when excluded from the air, or when heated in an atmosphere free from oxygen, in hydrogen gas for instance. Heated in contact with the air, no higher degree of oxidation is found to have taken place before the incandescence occurs, as with oxide of chrome, although Rose is obliged, from some experiments, to conclude that a higher degree of oxidation of titanium than titanic acid does exist. At times, when the titanic acid was heated for a long time, but not brought to redness, no incandescence occurred when the temperature was afterwards raised to redness. Neither the hydrated acid nor the acid heated to redness by means of a spirit-lamp exhibited any crystalline structure under the microscope, but appeared vitreous. It is known that titanic acid, precipitated by ammonia, is no longer soluble after ignition in diluted acids, and dissolves in concentrated sulphuric acid only upon being heated in it for a long time.

When titanic acid is dissolved in acids, and the solution diluted with water, the titanic acid, as is well known, is partially and at times completely precipitated by boiling the solution.

It is immaterial whether the titanic acid used for this purpose is one precipitated by ammonia and dissolved in a dilute acid, or an ignited titanic acid after its treatment with sulphuric acid, or after being fused with bisulphate of potash and solution of the fused mass, or a solution in an acid, procured by fusing any modification of titanic acid with a fixed alkaline carbonate; or lastly, a solution of chloride of titanium in water; for all these solutions contain the same modification of titanic acid. The separation of the titanic acid, which exists in the acid solution as a base, is occasioned by the water, which in this case acts as a stronger base, and precipitates it. The same effect which takes place in the precipitation of the oxides of bismuth, antimony and mercury in the cold, is exhibited in titanic

acid, oxide of iron, and many other weak bases, only upon heating them.

The precipitation of titanic acid by boiling its solution in hydrochloric acid diluted with water is not completely effected, but is perfectly successful when its solution has been effected in sulphuric acid and afterwards diluted, as Berzelius long ago remarked. A very long-continued boiling is however necessary to precipitate the whole. Titanic acid, thus precipitated, admits of being perfectly washed with pure water, even with hot water, without its passing milky through the filter, which, as is well known, is not possible with that obtained by boiling the solution in hydrochloric acid.

The titanic acid obtained by boiling its solution differs materially from that procured by precipitation by ammonia. It has lost its easy solubility in acids, is similar in that respect to the ignited acid, and is, like the latter, only soluble in sulphuric acid by long-continued heating.

These two modifications of titanic acid, that obtained by boiling and that by ammonia, behave to one another in the same manner as the two modifications of the peroxide of tin.

The titanic acid precipitated by ammonia is similar to the peroxide of tin precipitated from its solutions by ammonia, for instance from the perchloride of tin, in its easy solubility in dilute acids, and only differs from it particularly in admitting of being perfectly washed with water; which is not the case with peroxide of tin, as by continued washing it begins to be dissolved.

The titanic acid precipitated by boiling resembles the peroxide of tin thrown down by nitric acid, in being insoluble in weak acids. An important difference between the two modifications of titanic acid is exhibited on igniting them. That precipitated from its solutions by boiling exhibits no incandescence on ignition and remains white. When heated, it appears citron-yellow, but on cooling it becomes again white—a phænomenon exhibited by several metallic oxides. The acid precipitated by ammonia, on the contrary, always appears brown after ignition; and this brown colour is essential to it, as the colour of this after ignition is always more or less dark.

Titanic acid occurs in nature in *three* different forms, which, notwithstanding their variations, according to repeated examinations, were found by Rose to contain pure titanic acid, mixed with very little sesquioxide of iron (in rutile about 1 per cent., in the others still less). They are,—1st, *Rutile*, reddish-brown, behaves like ignited titanic acid, is not altered by exposure to the strongest heat, even in oxygen gas; specific gravity 4·239–4·255; 2nd, *Brookite*, differs from the former in its crystalline form, which belongs to the rhombic system; spec. grav. 4·128–4·165; it behaves also like ignited titanic acid; by continued ignition, however, its specific gravity increases to 4·17–4·19; 3rd, *Anatase*, which occurs of a blue, brown, and yellowish-red colour; the blue colour does not proceed from oxide of titanium; the powder is always white, and behaves like ignited titanic acid; mixed with charcoal, and heated to redness in chlorine gas, it gives liquid chloride of titanium; specific gravity 3·912–3·927;

by protracted red heat the specific gravity of anatase is increased gradually to 4·2, and upwards.

The remarkable increase of density, by heating to redness, here noticed, by which anatase and brookite seem to pass into rutile, takes place also in artificial titanic acid.

If titanic acid be precipitated by ammonia, the precipitate, perfectly washed, dried, and then by the flame of a spirit-lamp gently ignited for the shortest possible space of time, it has the specific gravity of anatase.

The titanic acid made use of by Rose in these experiments was prepared, partly from rutile, partly from iserine, or other varieties of titaniferous iron. The former was usually mixed in fine powder with bisulphate of potash and melted, and the fused mass dissolved in water; the latter were first melted with sulphur, and the fused mass treated with hydrochloric acid to free it from the greater portion of iron, after which the titanic acid was fused with bisulphate of potash and the fused mass treated with water. From these solutions the titanic acid was thrown down by continued boiling, and the precipitated titanic acid purified from a small portion of iron by treating it with hydrosulphate of ammonia, by which it became black, then with hydrochloric acid and well washing it. The titanic acid was then dissolved by heat in concentrated sulphuric acid, the solution diluted with much water, filtered, precipitated by ammonia, and the precipitate perfectly washed with cold water.

Titanic acid obtained by this method contains however an extremely minute quantity of oxide of iron. Larger quantities of titanic acid therefore should be precipitated, according to Berthier, from the solution in bisulphate of potash or sulphuric acid by ammonia, avoiding an excess of the precipitant, hydrosulphate of ammonia added, and gaseous sulphurous acid passed through until the titanic acid appears quite white, and then washed. Excellent as this method is, however, for preparing pure titanic acid, it is not applicable to analysis, for a portion of titanic acid is always dissolved along with the sulphuret of iron. The titanic acid obtained is redissolved in sulphuric acid, which occurs with evolution of sulphurous acid. If a considerable quantity of titanic acid be dissolved by heat in sulphuric acid in a platinum capsule, a very thick syrup is obtained, which may solidify to a tough mass. It dissolves easily in cold water, but not completely, unless an excess of sulphuric acid be added. From this solution, diluted with much water, the titanic acid is precipitated by ammonia in excess.

If titanic acid be ignited very gently in the manner mentioned above, the specific gravity fluctuates between 3·899 and 3·96. Some time ago, Rose once procured a titanic acid by precipitating with ammonia with a less specific gravity than anatase, viz. 3·655–3·66.

If titanic acid of the specific gravity of anatase be exposed to a strong and long-continued heat, its specific gravity is increased. Rose found that although a very high temperature expedited this effect, it could also be produced by a lower temperature long sustained, for he obtained nearly the same result by exposing the acid

to the heat of a spirit-lamp with a double current of air, as he did in the white heat of a powerful draught furnace fed with coke. In the former case, the specific gravity rose to 4·206, while in the latter its maximum was 4·210. It was in the end placed in the fire of a porcelain furnace. Hereupon it contracted strongly, but did not fuse, and became of a brown colour, as it did also at a white heat, very similar in colour to rutile.

The specific gravity of this acid was in whole pieces = 4·229; but this was still not the true density of this titanic acid, for although the pieces which had so strongly contracted had been boiled with water for a considerable time, they could not have been free from air, for the density of the powder was higher, viz. 4·244 and 4·254. This is the highest specific gravity that titanic acid can be brought to by heat. Rose believes also that the porcelain furnace produced this result less by the intensity of its heat than by its long continuance.

The titanic acid heated in the coke fire and that heated in the porcelain furnace had a much darker brown colour than that heated in the flame of the spirit-lamp, although the difference of specific gravity, with that heated in the coke-furnace at least, was trifling. This darker colour does not depend upon a minute quantity of titanic acid reduced to oxide of titanium, for the dark brown colour did not become lighter by ignition in an atmosphere of oxygen. The dark brown colour is that of rutile; but the titanic acid has become, by a violent and long-continued heat, rutile, which possesses the highest specific gravity of all the modifications of titanic acid.

Thus we see that the artificially prepared titanic acid by gentle ignition assumes the condition of anatase, and from this, by a strong and long-continued heat, passes through the modification of brookite into that of rutile.

A titanic acid precipitated from its solution in sulphuric acid by boiling, which had been heated until it became yellow only, had the specific gravity 3·671. It was prepared from rutile by fusion with bisulphate of potash dissolved in water, and the solution boiled until all the titanic acid was precipitated. The precipitate was then, after washing, treated with hydrosulphate of ammonia, and the sulphuret of iron formed removed by hydrochloric acid.

A titanic acid procured from iserine had a specific gravity of 3·955, similar therefore to anatase. The iserine was first melted with sulphur, and the greater quantity of the iron removed from the fused mass by hydrochloric acid, whereupon the titanic acid obtained was fused with bisulphate of potash, dissolved in water, precipitated by ammonia, redissolved in sulphuric acid, and fully precipitated from this solution by boiling. It contained rather more iron than the titanic acid used in the first experiments.

As the titanic acid is precipitated from its solution in sulphuric acid by boiling as a basic salt containing sulphuric acid, Rose ascribes the difference in colour from that precipitated by ammonia to a small portion of sulphuric acid, which is probably not entirely dissipated by heat. For the following experiments, therefore, the

acid precipitated from the sulphuric acid solution by boiling was edulcorated with ammonia, and after drying heated gently with carbonate of ammonia until it became yellow. It was then heated over the spirit-lamp until the bottom of the platinum crucible was of a dull red. On cooling it was perfectly white, but when moistened with water it swelled up considerably. It had a specific gravity of 3·882. It was free from sulphuric acid and iron. Another portion of titanic acid, prepared in the same manner, was of specific gravity 3·902.

This titanic acid was heated to a strong red heat by a spirit-lamp for half an hour. It lost half a milligramme in weight, had a very slight tinge of yellow, hardly perceptible on cooling, and no longer swelled up with water. Its specific gravity was 4·2074, approaching nearly therefore to that of rutile. The same titanic acid was exposed to a strong red heat in a charcoal fire. It did not change colour. Its density was 4·219. On exposing this titanic acid to the heat of a porcelain furnace, it experienced no alteration in weight; it had contracted, adhering slightly together, and its colour was yellowish; it was similar to the powder of ignited anatase; its specific gravity was 4·183.

It appears to follow from these experiments, that the titanic acid prepared by boiling is increased in density by a long-continued elevation of temperature, in like manner with that prepared by ammonia.

That the acid heated in the porcelain furnace should have a less specific gravity than that heated in a charcoal fire appears to be a fact, however, opposed to this view, but the experiment should be repeated. With brookite Rose found something similar.

If we take this for granted, however, the very different appearance of both kinds of titanic acid, and the white colour of that thrown down by boiling, are remarkable.

When titanic acid, precipitated by ammonia, washed with cold water, and dried under the air-pump thoroughly so as to aggregate into hard lumps, is moistened with concentrated sulphuric acid, the inner portions only, which were not touched by the acid, exhibit incandescence and become brown, while the outer portions do not exhibit this phænomenon and remain white.—Poggendorff's *Annalen*, vol. lxi. pp. 505–531.

On the Products of Decomposition of Phosphate of Magnesia. *By* L. Schaffner.

That the bibasic phosphate of magnesia was decomposed by ebullition with water had been pointed out by Riffault. The following experiments were undertaken by the author with the view of examining this decomposition with greater accuracy.

The salt used for analysis was obtained by mixing cold dilute solutions of phosphate of soda and sulphate of magnesia. If the salt is to be procured in the crystalline state, it is especially requisite that these conditions be enforced. If the liquid is set aside for 24 hours, silky needles are deposited; these are perfectly tasteless,

and nearly insoluble in cold water. The salt was dried, at the ordinary temperature, over sulphuric acid.

0·603 left, at 212°, 0·176 or 29·18 per cent. of water.
0·520 left, at 212°, 0·150 or 28·82 per cent. of water.

On exposure to a temperature of 356°—374° more water was liberated, and in two analyses the loss amounted to 21·50–22·00 per cent. On exposure to a red heat, the substance further lost 3·5 per cent.

The phosphoric acid was first combined with lead; the phosphate of lead was then decomposed by sulphuric acid and alcohol, and the phosphoric acid calculated from the loss. The magnesia was precipitated in the form of phosphate of ammonia and magnesia.

From analyses conducted in this manner, the following composition was elicited:—

PO^5, 2MgO, HO + 6 aq. + 8 aq.

	Calculated.	Found.
PO^5	28·98	29·32
2MgO	16·23	16·68
HO	3·65	3·50
6HO	21·90	21·75
8HO	29·20	29·00

The salt was now finely powdered and boiled with water. The supernatant fluid strongly reddened litmus, and at the same time deposited a heavy powder. The boiling was continued, the water being frequently replaced by fresh, until no more reddening of litmus paper ensued. The boiling required to be continued for a long time, for even after long-continued ebullition for several days, the liquid slightly reddened litmus. The residuary powder was now well-washed and dried. It formed a heavy insipid powder, insoluble in water, readily soluble in dilute acids, except the acetic, in which it was soluble with difficulty, and by which it differed from the original salt. When heated to redness, it continued to glow. Dried at 212°, it lost a small quantity of water, much less than an equivalent, which was therefore excluded from the calculation. At 356° it lost, on the average of two analyses, 23 per cent. of water. If the substance was now heated to redness, 9·10 per cent. more water was lost.

The phosphoric acid was again estimated, by dissolving the salt in dilute nitric acid, and then adding basic acetate of lead, until a slightly alkaline reaction was evident. The phosphate of lead and basic nitrate of lead obtained were heated to redness, whereby the latter was converted into oxide of lead, and then weighed. The phosphate and oxide of lead were then dissolved in nitric acid, and decomposed by sulphuric acid and alcohol; the sulphate of lead obtained was then washed and heated to redness. The oxide in this sulphate of lead was then calculated, and it was subtracted from that of the mixture of phosphate and oxide of lead previously obtained. The loss indicated the phosphoric acid. The magnesia was

estimated once from the loss, and a second time as phosphate of ammonia and magnesia. The per-centage composition was as follows:—

MgO	31·88
PO^5	37·00
HO	32·00
	100·88

The following formula may thence be developed:—

$$PO^5, 3MgO, 2HO + 5\,aq.$$

	Calculated.	Found.
MgO	31·43	31·88
PO^5	36·51	37·00
HO	22·90	23·00
HO	9·16	9·10

The liquid obtained by boiling the original salt was now strongly evaporated; but even after standing for a considerable time no crystals were deposited. The liquid was then evaporated over sulphuric acid *in vacuo*, and thus a glutinous mass, of a strongly acid taste, was obtained. When this was treated with strong alcohol, an insoluble powder was separated, and free phosphoric acid was found in solution. The salt was thus transformed into a basic compound, and free phosphoric acid; the latter retained in solution a portion of the undecomposed salt.

It was now attempted to obtain the acid salt by another method; and for this purpose phosphoric acid was saturated with carbonate of magnesia. If the solution which contained free phosphoric acid was mixed with a considerable quantity of absolute alcohol, a white powder separated, which was composed of 2MgO to $PO^5 + HO$, consequently the same as that obtained by the former method. If a small quantity only of alcohol is used, the same salt is separated in the form of oily drops, which at first taste very acid, but by drying crumble into the former powder. If completely neutralized, the phosphate of magnesia immediately separates, and in the supernatant fluid merely traces of phosphoric acid combined with magnesia are obtained. This salt, when boiled, undergoes the same change. Phosphate of zinc does not appear to undergo any alteration by boiling. Its composition is expressed by the following formula:—

$$PO^5 \left\{ \begin{matrix} 2ZnO \\ HO \end{matrix} \right. + 3\,aq.,$$

which contains 1 equiv. more water than Graham adopts in his Manual.—*Ann. der Pharm.* for April 1844.

On the Inorganic Constituents of Plants.
By MM. Wiegmann and Polstorff.

The following is Berzelius's report on the prize essay obtained by the authors at Göttingen in 1842:—

The authors sowed vetches (*Vicia sativa*), barley, oats, buckwheat, tobacco and clover, in two different soils. One was composed

of a white siliceous sand, from Königslutter in the neighbourhood of Brunswick, where the experiments were instituted. This was first heated to redness, to decompose as completely as possible all organic admixture, then digested for 16 hours with nitro-muriatic acid, then freed by washing from acid, and dried.

The other consisted of a mixture of sand which had been similarly treated, and the following substances, which were carefully weighed in:—

Sand	861·26
Sulphate of potash	0·34
Chloride of sodium	0·13
Sulphate of lime (anhydrous)	1·25
Fine chalk	10·00
Carbonate of magnesia	5·00
Oxide of manganese	2·50
... iron	10·00
Alumina (precipitated from alum)	15·00
Phosphate of lime	15·60
Humate of potash	3·41
... soda	2·22
... ammonia	10·29
... lime	3·07
... magnesia	1·97
... alumina	4·64
... iron	3·32
Humus, insoluble in water	50·00
	1000·00

The plants were watered with pure water, free from ammonia, and protected from external influences by being covered.

In the pure sand, they grew, shot up, but did not thrive; some flowered, others only partially; none bore fruit; the two diadelphous plants never once did so; in Boussingault's experiments however they did, although the soil contained no nitrogenous matter.

In the mixed soil, they grew up, flourished, flowered and bore ripe fruit containing perfect seeds.

A quantity of seed, equal to that which was sown, was incinerated, and the weight and composition of the ash ascertained. The plants obtained were pulled up when their growth seemed perfect, separated from matters adherent to their roots, dried and incinerated, the ash weighed and analysed. The analyses were performed by Polstorff, and appear to have been well executed. The general result was, that the ash of the plants sown in the sand taken altogether amounted to twice as much as that of the seed used, and sometimes even more. The plants grown in the mixture contained from 4–5 times, and even more than that, of the seed sown. The organic matter of the latter was $2\frac{1}{2}$ times as great as that of the former, and in the case of tobacco it was 5 times as great. To ascertain whence the double quantity of ash of the plants grown in the sand came, the boiled sand was analysed, and found to be composed of—

Silica	97·900
Potash	·320
Lime	·484
Magnesia	·009
Alumina	·876
Oxide of iron	·315
	99·904

After this sand had remained covered with water for a month, during which time carbonic acid was constantly passed into the latter, a solution had formed, which after evaporation was analysed, whereupon it was evident that silica, potash, lime and magnesia had been extracted; whence we easily perceive that here, as in ordinary soil, the sandy felspathic grains of the inorganic matter provide the grown plants with alkalies and earths, in consequence of a slight and slow decomposition. Wiegmann showed that the idea of the formation of these ingredients in the interior of the plants was incorrect, by sowing cress-seed in a mass of finely divided platina foil, and adding water to it. The cress grew well, but its ash weighed exactly as much as that of the seed which was sown.

The conclusion deducible from these experiments is, that these inorganic matters are necessary for the organization of the plants; that when these are deficient they wither, although it is quite possible that the whole amount contained in the ash is not absolutely indispensable for the formation of the plants. It is also probable that soda, potash, lime, magnesia, iron and alumina, as in the mineral kingdom, may replace one another if the soil contains more of one than of the other.

These beautiful and instructive experiments would have become more so, had a third comparison been instituted, *i. e.* had a portion of the sand been moistened with humus and humate of ammonia only; for it appears certain that the plants in the pure sand suffered from want of other nourishment than air and water; wherefore the experiment does not completely justify the conclusion drawn from it.—*Jahresbericht*, xxiii. pp. 312–315. *Pharm. Cent. Blatt.* for July 1844.

Examination of the Flesh of a Mummy.
By MM. Girardin and Preisser.

The product examined was removed from a corpse interred in St. Peter's church at Caen. It was the solid residue of the decomposition of the soft parts; a porous, pulverulent, reddish-black substance, containing grayish-white portions of carbonate and phosphate of lime, which were with difficulty incinerated, evolving an ammoniacal odour, and leaving 39 per cent. of ash (some lead it contained was derived from the coffin). Boiling water dissolved 2·72 per cent. of it, consisting of carbonate of potash, chloride of potassium and sodium, sulphate of potash, phosphate of soda, an ammoniacal salt, and traces of a substance precipitable in reddish-brown flocks by acids. Æther containing alcohol extracted 17·71 per cent., con-

sisting of an ammoniacal soap and a resinous substance insoluble in alkalies. Nitric acid in contact with it became of a dark red colour. Boiling dilute solution of potash dissolved 35·17 per cent., acquiring a brown colour, and the odour of ammonia being evolved. The solution yielded with acids a copious, bulky, reddish-brown, crystalline precipitate, when sufficiently purified by alcohol and water, much resembling Boullay's azulmine, and, in fact, like this consisting of C 50·23, H 1·68, N 47·90.

Quantitatively the flesh contained 10·4 water; 35·17 azulmine; 0·72 azulmate of ammonia, carbonate of potash, chlorides of potassium and sodium, sulphate of potash and phosphate of soda; 12·71 ammoniacal soap and resinous matter; 39·0 phosphate and carbonate of lime, carbonate of lead, silica and sand.—*Ann. de Chim. et de Phys.*, t. ix. p. 367.

Confervæ containing Iodine.

The Confervæ found in many thermal springs, mostly species of *Anabaina*, are used empirically as external applications to *goitre*, enlarged glands, &c. Henry has examined the Confervæ in the springs of Vichy, Neris and Vaux, and found small quantities of an alkaline iodide in each.—*Pharm. Cent. Blatt.* for July 1844.

Analyses of Blood. By Dr. Herrman Hoffmann.

These analyses were instituted upon specimens of diseased blood, collected by Dr. Scharlau. In the combustion, oxide of copper was used. The results are as follows:—

After subtracting the weight of ash, the organic substance yielded—

	Ash.	Carbon.	Hydr.
1. Blood of a patient affected with pneumonia, obtained by venesection, buffed	4·365	57·428	8·615
2. ... ... (another patient) also buffed	4·081	52·280	
3. A young man, pneumonia, V. S. 1.	3·880	51·966	8·543
3. A young man, pneumonia, V. S. 2.	3·784	51·149	7·832
4. Typhus	3·901	54·954	8·542
5. Tubercular phthisis, not buffed	4·026	53·734	7·451
6. Abdominal typhus, 5th day, V. S.	3·209	50·901	8·925
7. .. ... 2nd day, V. S. 1.	3·108	54·184	8·493
7. .. ... 2nd day, V. S. 2.	3·479	55·295	7·945
8. Typhus	4·702		
9. ... Vena Cava Inf.	3·509	49·281	7·217
10. ...	3·960	45·575	7·897
11. ... Blood of aorta.	4·184		

Ann. der Chem. und Pharm., April 1844.

Formation of Butyric Acid by the Fermentation of Potatoes.

When potatoes are bruised and washed in a sieve with cold water, a residue is left, which, when set aside in covered vessels at a tem-

perature not below 86°, begins to ferment, and which Scharling finds to be accompanied by a considerable formation of butyric acid. If the mass be treated, previously to fermentation, with a little carbonate of soda, and, when it is completed, with dilute sulphuric acid, the odour of butyric acid is developed. If it be treated with cold water, filtered, the filtered liquor evaporated, and the residue exhausted with alcohol, the butyric acid and acetate of soda are dissolved. If the evaporated solution is distilled with sulphuric acid, a concentrated aqueous solution of butyric acid first passes over. If the alcoholic solution be distilled with sulphuric acid, the distilled liquor smells of rum.—*Ann. der Chem. und Pharm.* for March.

On some Salts of Cupric Acid. By M. Kruger.

According to the author, the lime salt of cupric acid, which has hitherto not been isolated, is obtained on adding nitrate of copper to some pure chloride of lime mixed in water. At first a greenish, subsequently carmine-red precipitate forms, which becomes blue by standing, or on filtration and edulcoration with evolution of oxygen, and passes into the hydrate of the oxide of copper. Half an ounce of nitrate of copper, treated with chloride of lime, produces within 24 hours more than a quart of perfectly pure oxygen. It was not found possible to prepare other salts from this lime salt by double decomposition. Free acids disengage chlorine, it being impossible to remove the chloride of lime. The barytes salt is obtained from hypochlorite of barytes in the same manner as the lime salt. The potash salt (and soda salt) is obtained by passing chlorine through a solution of caustic potash, in which hydrate of copper is suspended until a disengagement of gas is perceived. It forms a beautiful red solution, which however is soon again decomposed with disengagement of oxygen and deposition of black oxide of copper. No cupric acid could be obtained by means of galvanism, as with ferric acid.

Hydrated oxide of manganese, treated with caustic potash and chlorine, affords hypomanganate of potash; the hydrate oxide of chrome gives chromate of potash, oxide of lead gives superoxide of lead, and oxide of zinc does not change perceptibly.—Poggendorff's *Annalen*, 1844, No. 7.

On a Combination of Prussic Acid with Oil of Bitter Almonds. By C. Völckel.

This compound is obtained on mixing water of bitter almonds with muriatic acid, and evaporating somewhat below 212°. It separates on cooling, when the liquid has been reduced to a small volume, in the form of a yellowish oily body, which should be shaken several times with distilled water, to purify it from adherent muriatic acid; upon which it is placed for a time under the air-pump over concentrated sulphuric acid, to remove every trace of water. This body curiously enough has scarcely any odour; it is not altered by expo-

sure to the air, dissolves with difficulty in water, but readily in alcohol and æther; the aqueous solution has a neutral reaction, and possesses a bitter taste; its specific gravity = 1·124; on exposure to heat, it is already partially decomposed at 212°, and completely at 306° Fahr., into oil of bitter almonds and prussic acid. With potash, it affords cyanide of potassium and oil of bitter almonds; evaporated with concentrated muriatic acid, it produces amygdalic acid and ammonia (with the assimilation of 3HO). It contains 71·98 C, 5·34 H, 11·01 N, 11·67 O, which corresponds to the formula $C^{14} H^6 O^2 + C^2 NH$, representing 1 atom of oil of bitter almonds and 1 atom of prussic acid.—Poggendorff's *Annalen*, 1844, No. 7.

ANALYTICAL CHEMISTRY.

Action of some of the Alkaline Salts upon the Sulphate of Lead. *By* J. Lawrence Smith, M.D.

It has been for some time known that certain neutral salts possess the property of dissolving to some extent the sulphate of lead, which property belongs neither to the acids or bases constituting these salts. By referring to Berzelius's 'Chemistry,' it will be found that the acetate and nitrate of ammonia are among the number. "1 part of the sulphate was dissolved in 47 parts of a solution of the acetate, of spec. grav. 1·036; and in 172 parts of a solution of the nitrate, of spec. grav. 1·144." In the 'Annalen der Chem. und Pharm.,' vol. xxxiv. 235, will be found the following statement:—"Sulphate of lead is easily dissolved, and in a large quantity, by a solution of neutral tartrate of ammonia. A concentrated solution forms after some time a stiff jelly, like silica." This last is no doubt a double tartrate of lead and ammonia.

I had also observed, some time previously, that a solution of the citrate of ammonia, when poured upon the sulphate of lead and allowed to stand, altered the character of the sulphate; and this, with the other fact above stated, led to the examination of what was really the action of these as well as other ammoniacal salts in general, upon the sulphate in question, and it was found that in every case it was decomposed.

Citrate of Ammonia.—If a solution of citrate of ammonia be poured upon the sulphate of lead and shaken together, the clear solution will be found to contain the sulphate of lead, as shown by hydrosulphuric acid, and a salt of baryta (taking care in testing with the baryta to acidulate first with pure nitric acid, to prevent the formation of the citrate of baryta). If they be allowed to remain several weeks in contact, the solution will be found to contain more lead, the sulphate having undergone decomposition, sulphate of ammonia and a double citrate being the result; as this latter salt is not very soluble, a large portion of it remains in the form of a precipi-

tate. The rapidity of this change is in proportion to the concentration of the solution of the citrate. If, instead of performing the experiment in the cold, we boil a tolerably concentrated solution of the citrate with the sulphate of lead, a very large quantity of the latter will be dissolved, and the solution become perfectly transparent. If it be set aside and allowed to cool, in the course of a few hours an abundant white precipitate will be formed, and upon testing the clear solution, sulphuric acid, ammonia, citric acid and oxide of lead will be found present. The precipitate, when washed, affords citrate of lead and ammonia. I was at first inclined to think it simply a citrate of lead, attributing the ammonia present to some of the citrate not washed out; but from its possessing certain characters which do not belong to the simple citrate, I consider it a double citrate of lead and ammonia. It contains not the slightest trace of sulphuric acid. It was not analysed, from the difficulty of obtaining it perfectly pure, as the water used to wash it decomposes it, and as yet this difficulty has not been surmounted. So then the result of the action of the citrate of ammonia upon the sulphate of lead is, first to dissolve it, and subsequently to decompose it, forming the sulphate of ammonia and citrate of lead and ammonia.

Tartrate of Ammonia.—If a solution of this salt be added to the sulphate of lead and shaken with it in the cold, the clear solution will be found to contain both lead and sulphuric acid; and if set aside for a few weeks the precipitate will have changed its character, having assumed a crystalline nature; the solution will no longer contain lead, but the quantity of sulphuric acid present will be found to have increased. The precipitate now consists of tartrate instead of sulphate of lead, which is completely soluble in dilute nitric acid, affording no precipitate with a salt of baryta. If the mixture of the tartrate and sulphate be boiled, this change takes place more rapidly, and in a manner somewhat different from the case of the citrate; the sulphate will not be dissolved in such large quantities; and moreover by continuing to boil the solution after the sulphate has been completely dissolved, the tartrate forms during the ebullition, and is precipitated in little shining crystals. If the ebullition be continued a sufficient length of time, the whole of the lead previously dissolved will combine with the tartaric acid. This is different from what takes place with the citrate, which when boiled upon the lead salt dissolves it, and no length of ebullition will produce a precipitate. The action of the tartrate is first to dissolve the sulphate, decompose it in part, and form a double tartrate of lead and ammonia, which last salt is subsequently decomposed by continued contact with water, or still more rapidly by its solution being boiled.

Acetate of Ammonia.—This salt also dissolves to some extent the sulphate of lead, but not so readily as either of the above salts. If the solution be boiled and evaporated to dryness, crystals of sulphate of ammonia are obtained, and an uncrystallizable salt of lead, probably an acetate of lead and ammonia. From the difficulty of separating the sulphate of ammonia from it, it is impossible to pronounce positively whether it is a double salt or simply an acetate of lead.

We see in this reaction the existence of a soluble salt of lead and the sulphate of ammonia simultaneously in the same solution, without a precipitate being formed.

Oxalate of Ammonia dissolves but slightly the sulphate of lead, owing no doubt to the impossibility of forming a double salt; but it will nevertheless decompose largely, the sulphate furnishing the oxalate of lead.

Muriate of Ammonia, if boiled with the sulphate of lead, will decompose it instantaneously, furnishing the chloride of lead and sulphate of ammonia.

The *Nitrate of Ammonia* does the same, forming nitrate of lead and sulphate of ammonia.

The *Carbonate* and *Succinate of Ammonia* produce similar effects.

The action of most of the corresponding salts of potash and soda was examined, and with very similar results. The fact is, it would appear that those alkaline salts which dissolve the sulphate of lead, decompose it, without reference to the time occupied in the solution, as in the case of the carbonate of ammonia, which decomposes the sulphate at the very instant of its solution; and it is impossible to detect, at any one time, other than a trace of lead in solution, whereas the quantity of sulphuric acid is constantly increasing.

The explanation is clear. The sulphate of lead is a salt with a strong acid and feeble base; the alkaline salts used contain feebler acids and stronger bases; they dissolve the sulphate, thus affording an opportunity for the acids and bases to act upon one another under favourable circumstances, and to follow a natural law in chemistry, the stronger acid combining with the stronger bases, and *vice versâ*.

From the above facts, some important hints might be afforded to analytical chemistry; for it will be at once seen that the presence of any of the alkaline salts in a solution from which it might be wished to precipitate lead in the form of a sulphate, would affect the accuracy of the result. What is true of the sulphate of lead may be found also true for other insoluble salts. Moreover, this shows the importance, in the analysis of mineral waters for instance, of weighing well the relative strength of the various acids and bases therein found, in order to ascertain what salts are present, and not to be contented with evaporating the water to dryness, and considering such salts as remain to be those existing in the water, for many of them may be formed during the evaporation. It is not at all improbable, that before many years the examination of mineral waters will be based as much upon calculation as upon analysis, the former of course being guided by the latter, and by certain laws not yet developed.—Silliman's *Journal* for July 1844.

CHEMICAL PREPARATIONS.

On the Preparation of Succinic Acid, and on the Production of Camphor by the Action of Nitric Acid on Amber. By O. Döpping.

Long ago it had been observed, in the preparation of succinic acid from amber, that the amount of acid might be increased in a certain degree by the addition on distillation of a small quantity of concentrated sulphuric acid. Sulphuric acid, as we know, is decomposed, when heated with organic bodies, into sulphurous acid, which is disengaged, and into oxygen, which finds its use in most cases. This circumstance led me to presume that the increased amount of acid is in part a product of oxidation, derived from the action of the oxygen, which separates from the sulphuric acid, on one of the principles of the amber; an action analogous to that of nitric acid on stearic and oleic acids, which, according to the observation of M. Bromeis, also gives birth, amongst other products, to succinic and suberic acids. With this end in view, I submitted a certain quantity of amber to distillation with nitric acid, of the strength of that which is generally found in commerce under the name of *aqua-fortis*. The operation was conducted in a retort communicating with a recipient, but was not hermetically adapted; it was cooled with care during distillation. The action of nitric acid needs only to be sustained by a gentle heat, the action being very regular when the amber employed for distillation is in fragments of about the size of a pea or bean. The amber is by degrees transformed into a yellow viscous mass, friable when cold, and easily fusible, which covers the surface of the nitric acid; at first it swells greatly, but disappears by the continued action of the nitric acid. The liquid is then perfectly clear, and after having been evaporated to a syrupy consistence, must again be submitted to ebullition with nitric acid. This operation must be repeated several times, and the last time it is best to use a very concentrated nitric acid, because the last portions of the resinous matter, which the syrupy liquor still contains, is oxidized with great difficulty. The acid liquor is finally evaporated, over a slow fire, to the consistence of a thick syrup, and is then set aside. The thickened syrupy liquor changes by degrees (in a few weeks in my experiments) to a mass of small crystals. The best method of separating them from the mother-ley is to convey the whole mass on to a glass funnel, of which the superior orifice of the socket has been slightly stopped with asbestos. The liquor which runs from the crystals is again oxidized by strong nitric acid and evaporated; a liquor, filled with little crystals, is obtained as at first, which is separated in the same manner. A third crystallization is also obtained, by treating afresh with nitric acid and evaporating the liquor separated from the crystals.

The crystals are then heated with strong nitric acid, which does not alter them, but destroys their impurities; for this purpose a quantity of nitric acid nearly equal to that of the crystals is employed. The crystals are obtained white after the cooling of the

acid liquor; they are purified by several crystallizations. They are in the form of white prisms, and taste like succinic acid. Heated on platinum foil, they melt and then volatilize without residue, diffusing vapours which excite coughing; they are very soluble in water and in alcohol; neutralized with ammonia, they produce no change in a solution of sulphate of lime, and behave generally like pure succinic acid.

By this process I obtained 15 grms. of pure succinic acid from 180 grms. of amber, a proportion far more considerable than hitherto obtained by any other mode of preparing succinic acid from amber. Although there is reason to regard succinic acid as a product of oxidation of a principle of amber, yet no positive proof of this has yet been given; but I hope to resolve this question by a series of other experiments. The process above described is not applicable to the preparation of succinic acid in great quantity, because of the loss of the colophony, which is employed in the arts, and on account of the price and quantity of nitric acid required.

During the distillation, the liquor contained in the recipient is of a green-blue colour, such as is observed when a mixture of nitrous and of nitric acid is diluted with water; after a little while this colour disappears, and the liquor differs little in smell and appearance from dilute nitric acid. But if this acid be neutralized with a solution of caustic potash (carbonate of potash would easily occasion a loss from the effervescence), it becomes very hot, and after the disappearance of the acid smell there is a strong and decided smell of camphor. If the liquor be agitated with æther after it has become cool, and then poured into a bottle, so placed that the æther may collect in its neck in a layer easy to be removed by means of a pipette, from the top of the liquor situated inferiorly, a crystalline residue is obtained on a watch-glass after the spontaneous evaporation of the æther, which may be freed from moisture by gentle pressure between folds of blotting-paper; it is pure crystalline camphor, which resembles the camphor of the *Laurus camphora*, L., in all its physical properties, and cannot be distinguished from it. Too much æther should not be used for the extraction of the camphor, because during its evaporation it carries away a part of it.—*Annal. der Chem. und Pharm.* for March.

Poudre Métallique.

This is a secret preparation sold in Paris for stopping teeth. It is surrounded by mercury, which is pressed away previous to application, when ammonia is disengaged, and the residue hardens to a solid metal. It appears to be an amalgam of silver and ammonia.

Gauger's Tooth Balsam for filling Hollow Teeth.

The following is the composition of this balsam:—2 oz. of mastic are dissolved in 3 oz. of absolute alcohol, the solution poured off from the sediment, and then 9 oz. of dry balsam of Tolu dissolved

in it with the assistance of a little heat. It is allowed to stand for some time in a warm place, and the balsam then distributed into small wide-mouthed bottles. It is applied by means of cotton.—Buchn. *Repert.*, vol. xxxiii. p. 211.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Mode of engraving upon or ornamenting Steel and other Metals by means of Electricity. By Mr. J. H. Pring.

The means which I propose consist of an application of electricity, which I believe to be new, and shall be happy if they prove to be of practical utility.

The manner in which I have succeeded in producing marks or sketches upon plates of steel is as follows:—

I united six batteries of the kind invented by Mr. Smee, in each of which the size of the plate of platinized silver was about 3 square inches. I fixed the plate of steel to be engraved upon at the zinc end of the batteries. Having placed a wire of considerable length, covered with silk, between the plate of steel and the zinc, I took hold of the wire in communication with the platinized silver, and used it as an etching point upon the plate of steel. A bright electric spark, accompanied by a slight attack upon, or bite into the steel, was the result each time the wire came in contact with the plate.

The wire, which served as a graver, was made of platina; the part which I took hold of was enclosed in a glass tube, in order to facilitate its being taken hold of and moved more easily, and to protect the hand against the electric shocks to which it would be exposed without this precaution.

On using the wire, in communication with the zinc, as an etching point, and attaching a plate of steel to the platinized silver, a totally different effect is produced. With the apparatus thus arranged, the spark resulting from the contact of the wire with the plate of steel is accompanied by the deposition of a very small portion of the wire itself upon the steel. By employing wires of different materials, such as gold, silver, platina, &c., a variety of ornamental designs may no doubt be produced upon surfaces of polished steel.

The effects of the electrical influence above described are not confined to steel; a nearly similar result may be obtained by substituting plates of any other metal. It is to be presumed, that by augmenting the quantity and intensity of the electric currents, the effect upon the steel or other metal would be proportionably greater; and it is very probable, that by modifying the process, the application thereof might be advantageously extended.—*Bulletin de l'Industrie.*

PATENT.

Patent granted to Wilton George Turner, Gateshead, Durham, *for the manufacturing of Salts of Ammonia and Compounds of Cyanogen.*

The nature of this invention consists in the application of guano for the purpose of producing salts of ammonia, that is to say, muriate and sulphate of ammonia, and compounds of cyanogen, that is to say, prussiate of potash and of soda, and prussian blue.

The author first describes his method of producing both salts of ammonia and compounds of cyanogen from guano by one process; the salt of ammonia in this case being the muriate of ammonia, or sal-ammoniac, and the compound of cyanogen being ferrocyanide of iron, or prussian blue. This is effected by subjecting the guano, in its state as imported, to destructive distillation in close vessels, the products of the distillation being conducted into water. A convenient method of operating for this purpose is to use iron retorts, similar to those commonly used for making coal-gas, and similarly arranged and connected by pipes with what is commonly known as a Woulfe's apparatus, by which the gases evolved by the distillation may be made to pass two or three times through water before escaping into the air. This apparatus may be formed of large wrought iron vessels, connected by cast iron pipes; they ought also to have an open pipe passing through the top, and trapped by the water in the vessels to serve as safety-valves; they must also be furnished with convenient tops for filling and emptying them. A series of three vessels will be sufficient, or even two close Woulfe's jars, the third being an open water cistern. The products of the destructive distillation, which should be conducted at a low red heat, but which temperature must be increased towards the close of the operation, consist principally of hydrocyanic acid and carbonate of ammonia, and carburetted hydrogen. These being conducted into the Woulfe's apparatus, the first two are rapidly absorbed by the water, and a strong solution of hydrocyanate of ammonia and carbonate of ammonia is formed. The ammoniacal solutions should be removed from the first receiver of the Woulfe's apparatus, and replaced by water, after the distillation is complete, if it be found that much ammonia has passed into the second receiver. As this is a criterion that the first water is saturated, the same course is true of the second receiver, as soon as the ammoniacal products begin to pass into the third. To this solution of hydrocyanate and carbonate of ammonia, removed from Woulfe's apparatus to convenient vessels, such as cisterns of wood, a solution of protomuriate of iron is added, in such quantities as shall yield sufficient iron for the conversion of the hydrocyanic into hydroferrocyanic acid and for the conversion of the latter into prussian blue, which is formed on the addition of muriatic acid in sufficient quantity to neutralize the free ammonia. The requisite quantity of muriate of iron is determined by testing a small portion of the liquor for hydrocyanic acid by the known methods; an excess is unimportant, as shown below. The precipitate

thus formed is now allowed to subside, and carefully separated from the solution. The precipitate, by being boiled with a solution of potash or soda, will yield the ferrocyanate of the alkali, which is obtained by crystallizing as usual. The solution should first be freed from any excess of iron it may contain by the careful addition of a fresh portion of the ammoniacal liquor, by which the oxide of iron will be precipitated and a neutral solution of muriate of ammonia obtained. The precipitated oxide and cyanide of iron having subsided, the solution of muriate of ammonia is drawn off by a siphon, and the sal-ammoniac obtained from it by the usual processes. The oxide of iron is added to the next quantity of hydrocyanate of ammonia. By the use of sulphate of iron and sulphuric acid, the sulphate of ammonia will be the ammoniacal salt produced, but the chemical changes and operations are similar.

The author then proceeds to describe his method of adapting the usual process of manufacturing prussiates or compounds of cyanogen when horn is the substance employed (namely, by burning it in fused potash), to the manufacturing of prussiates or compounds of cyanogen from guano. If, without any preparation either of the potash or the guano, the latter be used, as if it were dried blood or any of the ordinary matters employed in the manufacture of prussiates, it will be found that no prussiate is obtained, at least not until after a sufficient quantity of guano has been burnt away for the residuum to form the excess of carbon, which is required for the purpose, while, at the same time, the ammonia evolved is stifling. By the proper admixture, however, of carbonaceous matter with the guano, and by charging the potash with free carbon, the whole of the nitrogen may be converted into cyanogen instead of escaping as ammonia. The particular kind of carbonaceous matter used for mixing with the guano is unimportant; but the patentee prefers coal tar or pitch and a good clean coal. The tar is peculiarly beneficial, as it not only furnishes carbon, but binds together the dry powder of the guano, thus not only preventing the dry powder from being thrown out of the pot by the rapid combustion that is going forward, but from its tenacious qualities holding in the ammonia till it be decomposed by the fused potash. Innumerable mixtures may be found, all of which may be usefully applied; the following formula, however, has been found to be very advantageous:—Bring 42 lbs. of good Montreal ashes to a perfect fusion by a strong red heat. Add a mixture of 7 lbs. of coal and $3\frac{1}{2}$ lbs. of hæmatite in fine powder, in small portions at a time, and after it is well worked in allow the pot to gather its heat again. Now work in a mixture of 7 lbs. of guano perfectly dried, 7 lbs. of coal and $3\frac{1}{2}$ lbs. of tar. Then finish by working in 21 lbs. of guano, mixed with 10 or 11 lbs. of tar. The ball of metal or compound of cyanogen thus produced is as rich as those made from 42 lbs. of potash and 84 lbs. of horn, and should then be heated in the usual manner for turning it into prussiate of potash. It is obvious, if soda had been used in this process instead of potash, the compound of cyanogen obtained would have been prussiate of soda. —Sealed March 11, 1844.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on Asparagine. *By* M. Piria.

Towards the end of last winter, Dr. Menici of Pisa sent me a crystallized matter, which he had just extracted from the climbing vetch, with the request that I would examine and determine the nature of it by analysis. This sample did not seem to be sufficiently pure to be submitted to analysis; and the quantity being too small to allow of purification, I undertook to prepare the substance myself, that I might be able to submit it to a careful investigation.

I sowed about 10 lbs. of seed in a closed chamber, the floor of which was covered with vegetable mould. The germination took place, the light being excluded, and the plants soon grew to a considerable height. I then gathered them, expressed the juice, and submitted it to evaporation; first of all I observed the coagulation of a great quantity of albumen; the liquid, somewhat evaporated, and left to itself, deposited a mass of crystals of the substance in question. The evaporated mother-liquors afforded a fresh crop of crystals. The substance was brown, and weighed about 240 grms. Purified by repeated crystallizations and by means of animal charcoal, it gave definitively 150 grms. of a perfectly crystallized white matter, in the form of prismatic crystals, similar to those of sugar-candy.

The characters of this body, and especially the facility with which it disengaged ammonia under the influence of alkalies, led me to suspect its identity with asparagine, which was confirmed by analysis. I obtained—

Carbon	31·80
Hydrogen	6·85
Nitrogen	42·54
Oxygen	18·80

The purity of the product thus obtained, its abundance, and the simple means of extracting it, lead me to think that the method of preparation just described will hereafter be adopted by chemists as preferable to every other. Independent of the discovery of this new source of asparagine, there are some important questions of chemical physiology connected with the experiment which I have described. We may ask,—1st, if the absence of light is indispensable to the pro-

duction of asparagine; 2nd, if the asparagine pre-exists in the seed, or whether it is produced during the act of germination; 3rd, what part asparagine performs in the œconomy of the plant.

It is in the hope of throwing some light on these questions that I undertook the investigations, the principal results of which are the subject of this notice. I treated some seed, and some plants arising from the germination of these under the influence of light, by a process analogous to that which has been described. The seed did not supply the least trace of asparagine; the plants, on the contrary, gave it in abundance. Lastly, I submitted some plants, gathered at the period of flowering and fructification, to the same treatment; but the liquor, even highly concentrated, did not furnish crystals; however at a certain period of the evaporation an abundant deposition of a salt of lime was formed, the acid of which seemed to me to be new. We may then conclude that the seed of the vetch does not contain asparagine, and that this matter is developed in the act of germination, either in the light or in the dark, to disappear again when the plant flowers.

The production of asparagine in the dark proves that this matter does not derive its elements from the atmosphere, as is the case with so many other products which originate in vegetables under the influence of light. It is probable that a nitrogenous substance (perhaps caseine) exists in the seeds in question, which is transformed into asparagine, and into other products, during germination.

Led by these views, I undertook comparative researches on the composition of the seeds, and the plants which originate from them, at the different periods of their development. I will make known the results of my experiments as soon as they are terminated; for the present, I publish the principal facts observed, in order to ensure priority.

When asparagine is not perfectly pure, it soon changes directly even in its aqueous solution; after a few days a kind of fermentation takes place in the liquor, which totally decomposes the asparagine. The surface of the liquid is covered with mould, and the liquor exhales the insupportable odour of decomposing purulent matters. The same change is manifest when a certain quantity of juice extracted from the plant is added to a solution of pure asparagine. In every case, at the end of a few days, the whole of the asparagine has disappeared, and in its place we find *succinate of ammonia.*

This last fact seemed to me important enough to be confirmed by analysis. I prepared a fresh quantity of succinate of ammonia by the same process and on a greater scale; I then transformed it into succinate of lead; this, decomposed by sulphuretted hydrogen, afforded a liquor from which I extracted pure crystallized succinic acid. The analysis gave—

	Found.		Calculated.
	I.	II.	
Carbon.....	40·27	40·4	40·67
Hydrogen	5·28	5·1	5·08
Oxygen	54·45	54·5	54·25

To explain the transformation of the asparagine into succinate of ammonia, we may suppose the pre-existence of succinic acid in the asparagine and its production by a disintegration induced by the fermentation. But this view of the subject seems improbable to me. I rather think that the crystallized asparagine, the formula of which only differs from that of succinate of ammonia by 2 equiv. of hydrogen, takes this hydrogen from the putrifying matters by virtue of an action analogous to the transformation of blue indigo into white indigo, under the reducing influence of the organic matters undergoing putrefaction.

I hope however to resolve this question by direct experiments.—*Comptes Rendus*, Sept. 16, 1844.

On a new Class of Salts. *By* Ed. Fremy.

Several able chemists have examined with care the action which the oxygenized compounds of nitrogen exert on sulphurous acid. It is to their united investigations that the actual mode of manufacturing sulphuric acid is due.

It is also known that M. Pelouze described, in his Memoir on the Nitrosulphates, the composition and properties of the salts resulting from the absorption of the deutoxide of nitrogen by the sulphites. But the action of nitrous and hyponitric acids on the sulphites has hitherto not been investigated. It is this question which is treated of in the following Memoir, and it is connected, as will be seen, with the important history of sulphur and of nitrogen.

In the present communication I shall suppress the details of the experiments, and shall merely give the principal characters of the new bodies which I have discovered, and point out their theoretical importance.

When sulphurous and nitrous acids are passed into a concentrated solution of potash, the two acids do not decompose each other, as would have been expected, so as to form a sulphate and deutoxide of nitrogen, but, on the contrary, combine and give origin to a new acid containing the elements of sulphurous acid, of nitrous acid and of water, and which is consequently formed of oxygen, sulphur, nitrogen and hydrogen. To this new acid I have given the name *sulphammonic*, which calls to mind its composition and its characteristic property of being readily decomposed into sulphuric acid and ammonia.

The alkaline sulphammonates may be obtained by passing sulphurous and nitrous acids into an alkaline solution. The nitrous acid is obtained from the action of nitric acid on starch. Hyponitric acid acts in this circumstance like nitrous acid. The sulphammonates may likewise be formed by mixing solutions of a sulphite and a nitrite. But the best process for preparing these new salts consists in causing sulphurous acid to act on a nitrite which has been previously rendered very alkaline. Few salts are prepared with greater facility, for in a few hours many hundred grammes of crystallized sulphammonate of potash or ammonia may be obtained.

I will now pass on to the examination of the principal sulphammonates.

Sulphammonate of Potash.—When a current of sulphurous acid is passed into nitrate of potash, the liquor soon becomes turbid, and deposits long silky needles of sulphammonate of potash, which is scarcely soluble in alkaline water. This salt may likewise be prepared by double decomposition, by treating the sulphammonite of ammonia with a potash salt.

The sulphammonite of potash is white, sparingly soluble in cold water; 1 part water at the ordinary temperature dissolves only one-fiftieth. It has no action on coloured test paper, no taste, and presents none of the characters of the salts formed by the acids of sulphur or of nitrogen.

The equivalent formula for the sulphammonate of potash exhibits its principal reactions; it is $7SO^3$ (SO^2, NH^2), 4KO + 3HO. It contains therefore an acid, which may be considered as a combination of sulphuric acid with sulphamide.

Some chemists admit that the compound SO^2, NH^2 can combine with sulphuric acid to form complex acids; the sulphammonic acid belongs to this new class of acids, to which MM. Laurent and Persoz have recently called attention.

It was easy to foresee the decomposition which water would cause on the sulphammonate of potash; it is, in fact, evident that the elements of water suffice for its transformation into acid sulphate of potash and sulphate of ammonia. This transformation of the sulphammonates into sulphates and ammoniacal salts is certainly the prominent character of these new compounds. When sulphammonate of potash is boiled for some seconds in water, the liquid, which was perfectly neutral, immediately acquires an acid reaction, and contains in solution nothing further than acid sulphate of potash and sulphate of ammonia. I shall subsequently describe the decomposition which cold water produces in sulphammonate of potash. This salt keeps for some time without decomposition when dry, but with time the water of crystallization which it contains decomposes it into sulphate and into ammoniacal salt.

The crystals of sulphammonate of potash, heated to redness, give all the products of decomposition of the sulphate of ammonia and of the bisulphate of potash.

Sulphammonate of Ammonia.—The analysis of this salt has entirely confirmed the composition of the salt of potash; it is represented by the formula $7SO^3$ (SO^2, NH^2) 4(NH^3, HO). This salt is produced in the reaction of sulphurous acid on nitrite of ammonia; it is white, much more soluble in cold water than the potash salt, and is decomposed under the same circumstances into acid sulphate of ammonia. An excess of ammonia renders it more stable. The potash salt may be prepared from it by double decomposition, in which case it is precipitated in long nacreous needles.

The sulphammonates of barytes, strontia, lime, &c., may be prepared by double decomposition. They are sparingly soluble in cold water, and are deposited in the state of a crystalline powder. It is

difficult to dry them; the salts frequently decompose spontaneously into sulphate, sulphate of ammonia and free sulphuric acid. The sulphammonate of soda does not appear to form with facility; the sulphammonate of lead is prepared by double decomposition, in presence of a slight excess of ammonia. The other sulphammonates are soluble in water.

Sulphammonic Acid.—This acid may be isolated by treating the sulphammonate of barytes or of lead with dilute sulphuric acid. The acid so obtained is soluble in water, possesses a strong acid reaction and taste, and is able to reproduce the sulphammonates when brought into contact with the bases.

Sulphammonic acid is quickly converted in cold water into sulphuric acid and bisulphate of ammonia.

New Salts which result from the Action of Cold Water on the Sulphammonates.

I have stated above, that when the sulphammonates are boiled in water they are decomposed into sulphates and ammonia; before, however, arriving at this last stage of decomposition they pass through an intermediate state, which constitutes a series of new salts, the composition and properties of which I shall here briefly describe.

When sulphammonates are left for some hours in cold water, the liquid becomes strongly acid, contains a bisulphate in solution, and deposits a new salt presenting the greatest analogy with the sulphammonate, and which belongs to a new class of salts, to which I have given the name of sulphamidates.

Sulphamidate of Potash.—To prepare this salt the sulphammonate of potash is left in cold water for several hours, or treated with water at a temperature of 140° to 158°, which at first dissolves it, but subsequently beautiful crystalline laminæ are deposited of sulphamidate of potash. The mother-water is strongly acid, and retains some bisulphate of potash in solution.

The salt has for formula $5SO^3\,(SO^2, NH^2)\,3KO$, the sulphammonate being represented by $7O^3\,(SO^2, NH^2)\,4KO + 3HO$.

The analysis, the details of which I here pass over, prove that these two differ solely by 1 equiv. of bisulphate of potash. The sulphamidate of potash is white, sparingly soluble in water, which dissolves only one-sixtieth at the ordinary temperature; it has some characters in common with the sulphammonate, being like it decomposed in boiling water into acid sulphate of potash and sulphate of ammonia.

As the sulphamidate of potash contains no water of crystallization, it may be preserved for any length of time without alteration; when heated to redness it is likewise decomposed into sulphurous acid, ammonia and sulphur. The sulphamidate of ammonia is prepared by leaving the corresponding sulphammonate in cold water for some hours; it is a very soluble salt, crystallizes with difficulty, and may be considered as a good test for salts of potash, which it precipitates, forming a sparingly soluble sulphamidate of potash. It is decomposed by boiling water into acid sulphate of ammonia.

The sulphamidates of barytes, strontia, lime, &c., are prepared by double decomposition, and appear in general to be more stable than the sulphammonates.

Having thus described the new facts, I shall enumerate in a few words the theoretical consequences which result from these investigations. It is seen at first that nitrous and hyponitric acids exercise a very peculiar action on the sulphites, presenting no analogy whatever with that of the other oxygenized combinations of nitrogen; in fact, nitric acid converts the sulphites into sulphates and disengages red gas. The deutoxide of nitrogen is wholly absorbed by the sulphites, giving origin to the nitrosulphates; while nitrous and hyponitric acids form, by acting on the sulphites, a new series of acids, composed of sulphur, oxygen, nitrogen and hydrogen, and which, under the sole influence of water, are converted into sulphuric acid and ammonia. These bodies present an evident analogy with those which are produced in the combination of anhydrous sulphuric acid with ammonia, and which have been examined with so much care by MM. H. Rose and Jacquelain.

The production of ammonia in the reaction of nitrous acid on the sulphites is, I believe, a wholly unexpected fact, which nevertheless is connected with previous observations; it is known indeed that when nitric acid acts energetically on some metals or on certain organic substances, the production of ammonia is frequently observed. I would also call to mind that MM. Pelouze and F. Boudet have proved that hyponitric acid, when solidifying certain oils, produces a nitrogenous compound, which presents all the characters of an amide.

These facts will not remain isolated. I purpose showing, in a subsequent communication, that the nitrous and hyponitric acids ought not to be considered solely as agents of oxidation, but that the nitrogen contained in these acids may, on combining with hydrogen, form in some cases ammoniacal salts, and in others true amides.—*Comptes Rendus*, Sept. 16, 1844.

Cnicine.

This substance, which M. Nattiville obtained from *Centaurea benedicta*, occurs, according to M. Scribe, in all *Cynarocephalæ*. It crystallizes in transparent white needles, which have no smell, a bitter taste, are perfectly neutral, not affected by exposure to air, fuse and are decomposed by heat; it is little soluble in cold, more so in boiling water; the solution deposits, on long boiling, a tenacious body. Alcohol dissolves it readily, æther but sparingly. The substance consists of 62·9 C, 6·9 H, 30·2 O.—*Comptes Rendus*, xv. p. 808.

On the Silicic Æthers. *By* M. Ebelmen.

The action of absolute alcohol on the chloride of silicium has allowed of my preparing two well-defined combinations of æther with silica. They are produced under the following circumstances;—

On cautiously adding absolute alcohol to chloride of silicium, a very lively action ensues, accompanied by a very abundant disengagement of hydrochloric acid gas and a considerable lowering of temperature. When the amount of alcohol added has slightly exceeded the weight of the chloride of silicium, no more disengagement of gas is observable, and the liquor then becomes perceptibly heated. If the mixture be submitted to distillation, a certain quantity of hydrochloric æther first passes over, then the greater part of the liquid contained in the retort distils over between 320° and 338° Fahr. This first product is placed aside, and the distillation continued until above 572°. Only traces of silica remain in the retort.

The product, distilled between 320° and 338°, was rectified until its point of ebullition became constant between 323° and 325°. A colourless liquid, of an æthereal and penetrating odour and a strong peppery taste, of which the density is 0·932, was thus obtained. Water does not dissolve it, and decomposes it but very slowly, with a deposit of silica. It behaves perfectly neutral towards litmus-paper. Alcohol and æther dissolve it in every proportion. Alcoholic solutions of the alkalies decompose it rapidly, and the silica may be separated by means of the acids in the gelatinous state. On projecting some drops of it on to a capsule of red-hot platinum, it burns with a white flame, depositing silica in the state of an impalpable powder.

The analysis of this compound shows that the carbon and the hydrogen are contained in the same proportions in it as in æther, and that the silica contains the same quantity of oxygen as the base. If therefore we admit, with M. Berzelius and the generality of chemists, the number 277·32 as the equivalent for silicium, and SiO^3 as the formula for silica, the formula of the æther would be $SiO^3\ 3C^4\ H^6\ O$.

If, on the contrary, the third of the preceding number, or 92·44, be taken as the equivalent of silicium, and SiO as the formula of silica, as proposed by M. Dumas from the density of the vapour of chloride of silicium, the formula for silicic æther becomes similar to that of the other compound æthers, and is represented by $SiO\ C^4\ H^5\ O$.

Its density of vapour was found equal to 7·18; calculation gives 7·234, admitting that $SiO\ C^4\ H^5\ O$ represents 1 volume of vapour. This mode of condensation had not yet occurred in the compound æthers.

By receiving in separate portions the product distilled between 338° and 572°, and submitting them to analysis, we find that the carbon and hydrogen constantly occur in the same proportions as in æther, but that the proportion of silica increases with the temperature. The liquid distilled above 572° is colourless, and possesses a feeble smell and a taste quite different from that of the preceding æther. Its density is 1·035. The action of water and of the alkalies on this compound is quite the same as on the æther, $SiO\ C^4\ H^5\ O$. Its analysis leads to the formula $(SiO)^2\ C^4\ H^5\ O$.

Silicic acid therefore forms at least two æthers; and this fact, unique up to the present time in the history of these kinds of compounds, deserves to be compared to the existence of the numerous metallic silicates of different degrees of saturation, which occur in the mineral kingdom.

The formation of two silicates of ethyle, in the reaction of alcohol on chloride of silicium, is easily explained according to the two following formulæ:—

$$SiCl + C^4 H^6 O^2 = HCl + SiOC^4 H^5 O.$$
$$(SiCl)^2 + 2C^4 H^6 O^2 = C^4 H^5 Cl + HCl + HO + (SiO)^2 C^4 H^5 O.$$

In the action of the alcohol on the chloride of silicium, only hydrochloric acid is disengaged whilst the chloride is in excess; and it is only when the last portions of alcohol have been added, that it is possible to obtain hydrochloric æther. According to these formulæ, 575 (1 equiv.) of alcohol require 535 of chloride of silicium (1 equiv.), which were the proportions employed.

The action of alcohol on the chloride of silicium allows the hope that analogous experiments, made with the different alcohols and the volatile chlorides decomposable by water, may lead to the discovery of a great number of æthers formed by mineral acids, which it has hitherto been found impossible to prepare. I have already tried the action of alcohol on the chlorides of titanium, of tin, of phosphorus, of arsenic and of sulphur, and have obtained interesting reactions with several of these bodies, the examination of which I am following up, and shall hereafter have the honour of communicating to the Academy.—*Comptes Rendus*, p. 398, Aug. 19, 1844.

On a new Oxide of Chrome. *By* Eug. Peligot.

My researches on uranium have led me to study the products of the simultaneous action of chlorine and charcoal on several oxidized bodies possessing great stability, and which are only deprived of their oxygen under the combined influence of these two bodies. It will be remembered that it was this same action which allowed me to detect the existence of oxygen in *urane*, an oxide which was then considered to be a simple metallic body.

In this notice I propose making known some facts relative to the products which result from the decomposition of the green oxide of chrome by chlorine and charcoal. I shall shortly publish my investigations on this subject at length.

On passing a current of chlorine over a mixture of oxide of chrome and of charcoal, a chloride which sublimes in beautiful scales of a violet colour is obtained. This compound corresponds to the sesquioxide of chrome, $Cr^2 O^3$; its composition, as far as I have been able to verify it by new analyses, is represented by the formula $Cr^2 Cl^3$.

But this product is not the only chlorinated body which results from this operation; its formation is preceded by that of another chloride, which seems to have escaped the notice of chemists, and which presents itself in the form of very minute white silky crystals, generally mixed with some charcoal and some oxide of chrome.

These crystals become green directly they are exposed to the air, and in a few instants change into a green fluid; they at once absorb oxygen and water from the atmosphere. The analyses which I have made of this chloride leave no doubt as to its nature. It is composed of 1 equiv. of metal and 1 equiv. of chlorine, CrCl; it consequently corresponds to a degree of oxidation of chromium, CrO, till now unknown.

This same body originates when a current of hydrogen is passed over violet chloride of chromium heated to a dull red; hydrochloric acid is disengaged, and a white crystalline mass remains; by operating at a more elevated temperature, this mass fuses, and on cooling presents a fibrous texture. A German chemist, M. Moberg, studied in 1843 the action of hydrogen on the violet chloride of chromium; but he mistook the nature of the compound which resulted from this action, and did not obtain it in a state of purity. My experiments on the protochloride of chromium produced by chlorine, oxide of chrome and charcoal, date from 1842, as I can establish by the testimony of several chemists to whom I communicated the results of my analyses at that period.

The protochloride of chromium prepared by either of these processes presents the following properties:—Placed in contact with water, it immediately dissolves; if the water is aërated, and if the operation is performed in the presence of air, the solution is green. *It is blue* when the influence of oxygen is wholly avoided.

I know of no body which is more rapidly changed by the contact of oxygen than this compound. To study its reactions, it is therefore necessary to operate constantly with water deprived of air by ebullition, and in an atmosphere of carbonic acid.

The green solution which results from the action of the air and water on the protochloride of chromium possesses the singular property of dissolving a considerable quantity of the violet chloride of chromium with considerable disengagement of heat. This last-mentioned body, when pure, is wholly insoluble in water and in acids. This property of the white chloride, which habitually accompanies the violet chloride when this is prepared by the usual method, has thrown much uncertainty on the true characters of this latter body, which certain authors consider as very soluble in water and as producing a green solution; whilst others dispute its solubility, and with reason.

When the protochloride of chromium has been prepared from the sesquichloride by means of hydrogen, its solution in water is accompanied with a disengagement of hydrogen. This decomposition of water, which otherwise is not considerable, seems to indicate the existence of a subchloride, which would result, as does the subchloride of uranium, from the prolonged action of the hydrogen on the protochloride.

Potash gives, with the blue solution of the protochloride of chromium, a brown precipitate, which is probably the hydrate of the protoxide corresponding to this chloride; ammonia gives a precipitate of the same nature; an excess of ammonia furnishes a blue

solution, which under the influence of air becomes violet, and finally acquires a red colour.

The monosulphuret of potassium produces a black precipitate in the solution of the protochloride of chromium.

On adding to this same blue liquid a solution of acetate of soda or of potash, small red and transparent crystals soon make their appearance, and unite rapidly at the bottom of the vessel. These crystals are destroyed on exposure for a few instants to the air; but it is possible to obtain them sufficiently pure by employing certain minute precautions. They resemble, when dry, protoxide of copper. This body is the acetate of the protoxide of chrome, whose composition, according to four analyses, is represented by the formula $C^4 H^5 O^3$, CrO, HO.

The determination of the carbon of this salt, which I have made with the greatest care, has enabled me to submit the number representing the atomic weight of chromium to a rigorous test. I have every reason to think that the number is not exact; it is too high. I shall shortly communicate to the Academy the results on which this assertion is founded.

I have analysed another salt of protoxide of chrome, whose existence will probably throw much light on the nature of this oxide; it is a double sulphate of protoxide of chrome and potash, the composition of which is represented by the formula SO^3, KO + SO^3, CrO + 6HO, which is that of a large number of double sulphates. The protoxide of chrome is probably isomorphous with magnesia and several oxides of the same constitution. Chromium therefore would present the remarkable character of a threefold isomorphism; that of its protoxide, CrO, with the oxides just mentioned; of its sesquioxide, $Cr^2 O^3$, with alumina, peroxide of iron, &c.; of chromic acid, CrO^3, with sulphuric acid.—*Comptes Rendus*, Sept. 23, 1844.

ANALYTICAL CHEMISTRY.

On the Behaviour of Sulphur towards Metallic Solutions. *By* L. Freundt.

The property of sulphur to decompose metallic oxides when fused or boiled with them, and to combine generally with the reduced metals, while a part becomes oxidized to sulphuric or hyposulphurous acid, and unites with a portion of the undecomposed metallic oxide to a salt, has long been known. Sulphur, however, is likewise capable of decomposing metallic salts, and it requires neither double decomposition, as the employment of sulphuretted hydrogen, nor fusion. When well-washed flowers of sulphur are brought into contact with a solution of nitrate of silver, a reaction is perceptible on well shaking the liquid even at the ordinary temperature, and the sulphur acquires a gray instead of its yellow colour. When heat is applied, the action proceeds rapidly, and the colour of the

sulphur is very soon changed into black if too much has not been added. At a certain point the reaction ceases, and no further effect is observed on substituting a fresh quantity of pure flowers of sulphur for the altered ones, even after long boiling. The liquid has now an acid reaction. If it be neutralized with carbonate of lime or carbonate of barytes, the action again becomes perceptible on being heated, and the whole amount of silver can be converted, by long boiling, with renewed addition of sulphur and small quantities of carbonate of lime, into sulphuret of silver. Here, as under other similar circumstances, sulphuric acid is formed, with this difference that in other cases it combines with a base, while in the present instance it remains free. The process loses in simplicity by the addition of carbonate of lime, since that is alone capable of decomposing the silver salt, and consequently the decomposition can no longer be attributed solely to the action of the sulphur. However, the process proceeds even before the addition of the lime.

If a few drops of nitric acid are added to the solution of silver previous to the commencement of the operation, no decomposition of the salt takes place, and the circumstance that the silver cannot be wholly separated from the solution without the presence of some body to neutralize the acid, must therefore solely be ascribed to the excess of acid. Solutions of other metallic salts, which were experimented with, exhibited the following behaviour:—

Solution of sulphate of zinc undergoes no change.

Protosulphate of iron is not decomposed; the change of colour is owing to the separation of some peroxide of iron.

No effect is produced on the solution of sulphate of copper although carbonate of barytes decomposes the salt entirely and throws down the whole of the copper. When this has happened, and the liquid has now no longer any acid reaction, the sulphur begins immediately to act on the separated carbonate of copper, and continues as long as there is any copper salt, when carbonate of barytes is present.

Crystallized acetate of lead is not altered; with basic acetate of lead, on the contrary, the action commences immediately on boiling.

Arsenious acid undergoes no change even on the addition of carbonate of potash.

Pernitrate of mercury is not decomposed, while protonitrate very soon presents the formation of sulphuret of mercury.

Nitrate of bismuth and tartar-emetic are not changed.

It is evident that the acid reaction of the salts is principally of influence. Nitrate of silver and basic acetate of lead, the only metallic salts which do not react acid, are readily attacked by sulphur. If, with the protonitrate of mercury, an action takes place notwithstanding its acid behaviour, it must be ascribed to the slight affinity of the metal for the oxygen. The acid-reacting sulphate of copper is not affected; the insoluble carbonate, on the contrary, is readily decomposed. A small addition of acid to the first two salts prevents their being attacked, and only the protonitrate of mercury, notwithstanding the addition of acid, is acted on more or less.

Sulphur has no action on the soluble chlorides of iron, mercury and gold, although in the latter the affinity for the chlorine is but feeble. Salt of tin is readily decomposed; it changes its colour considerably, according to whether the acid soluble combination or the basic is brought into contact with the sulphur, and passes from brown-yellow into dark brown and violet. If, however, so much acid is added as is necessary to keep the solution clear, no reaction occurs as with the oxysalts.

According to these incomplete experiments, the behaviour of sulphur towards the metals is very characteristic, and might merit some attention in analytical chemistry.—*Archiv der Pharm.* for September 1844.

A Test for Bile.

M. Pettenkoffer, a German chemist, has discovered a test for the presence of bile. It consists in adding to the fluid supposed to contain bile concentrated sulphuric acid until it becomes hot, and then dropping into it a solution of sugar (syrup); the presence of bile is manifested by the mixture becoming of a deep pink or red colour, varying in intensity with the amount present.—*Lancet*, Oct. 5, 1844.

CHEMICAL PREPARATIONS.

Purification of Gum-resins by means of Distilled Water and Essential Oil of Turpentine. By M. Lamothe.

Various media have been successively employed for the purification of the gum-resins. Baumé recommends dissolving them in vinegar; the old French Codex substitutes white wine for vinegar; that of 1818, weak alcohol for the white wine; and in the preparation of *Empl. Conii*, it orders vinegar of squills and hemlock juice for dissolving the gum-ammoniac. The late M. Henri, in his lectures at the Pharmacie Centrale, likewise suggested weak alcohol as the best solvent; a method which has generally been adopted, and which is prescribed in the new Codex.

I confess that alcohol affords an homogeneous product well adapted for being incorporated in plasters; but if the length of time required for the operation be taken into consideration, the expense of the alcohol, which notwithstanding the care of the operator is for the greater part dissipated, and the quantity of the liquid requisite for dissolving completely the gum-resins, the preference will be given to the process which I have employed for sixteen years in my laboratory; a process which is less expensive, more expeditious, and affords equally good products:—

℞ Gum-ammoniac, or any other gum-resin.... 1 part.
Distilled water ..... 4 parts.

Macerate for 12 hours in a tinned copper basin, agitating now and

then with a wooden spatula: at the end of this time expose the mixture for some minutes to a temperature of 158° to 168°, strain through linen with slight pressure, treat the residue with a fresh quantity of distilled water and express, and subject it to a third and even to a fourth digestion, each time in 2 parts of distilled water. There remain a tenacious pitchy magma, which is exposed to a gentle heat in half a part of essential oil of turpentine and as much distilled water; the latter to dissolve the gummy portion, the former to dissolve the resin; strain with pressure. If the residue is not entirely exhausted, place it again over the fire with a fresh quantity of essential oil and water; mix all the liquids, and evaporate in the water-bath until all moisture is driven off, stirring constantly.—*Journ. de Pharm.* for August.

On the Preparation of the Valerianate of Zinc and its Medicinal Employment.

The valerianate of zinc, first proposed by Prince Louis Lucien Bonaparte as a medicine of considerable value, has for some years occupied an important place in the therapeutics of the Italian physicians. Dr. F. Devay, physician to the Hotel Dieu of Lyons, has recently made numerous experiments with this substance, the remarkable results of which have excited the attention of French practitioners to a high degree; and the valerianate of zinc has all at once got into great favour, so much so that for some weeks this salt is constantly being prepared by the principal pharmaceutists of Paris.

Under these circumstances a review of what has been published relating to the valerianate of zinc will undoubtedly interest many of our readers. Valerianic acid, discovered by Planche, was isolated by Grote, and was investigated by Penz. It preexists in the root of valerian, but it may likewise be readily produced by acting with caustic potash on potato fusel oil. It is a volatile fat acid, colourless, soluble in every proportion in alcohol and æther, and soluble in about 30 times its weight of water. To obtain it, the valerian root is distilled until the product has no longer an acid reaction; the essential oil which floats on the surface of the distilled water is separated, and the acid which it retains removed by shaking it with solution of caustic potash; the distilled water is saturated with carbonate of potash, the liquids mixed, and then evaporated to dryness at a very gentle heat; the residue, introduced into a retort and distilled with a suitable proportion of dilute sulphuric acid, affords a saturated aqueous solution of valerianic acid, on which some pure valerianic acid floats. 2 lbs. of valerian root afford about 2 grms. of acid.

To convert it into valerianate of zinc, it is saturated with the carbonate, or still better with perfectly pure oxide of zinc recently precipitated. The action is assisted by heat, the hot solution filtered and allowed to crystallize on a gently heated sand-bath. The crystals form light nacreous laminæ of a brilliant white colour. Ac-

cording to M. Duclos, cold water dissolves one-fiftieth of its weight and boiling water one-fortieth. It is scarcely soluble in æther, but 100 parts of boiling alcohol dissolve 6 parts.

Valerianate of zinc was recommended as an antispasmodic, and the experiments of Dr. Devay were undertaken to determine its value as such. The results which he obtained have been remarkable from the quickness and completeness of the cures. The physiological effects are scarcely more decided than those of the valerian or of the zinc taken separately. A dose of $2\frac{1}{2}$ grs., which is sufficient to subdue an attack of neuralgia or moderate the paroxysm of a violent megrim, produces in the healthy state but a little cephalalgia, slight vertigo, and a little confusion of hearing. It is particularly in the case of tic-douloreux, which cannot be subdued by the ordinary antispasmodics, that Dr. Devay has confirmed the efficacy of the valerianate of zinc; he has likewise applied it with success to the treatment of some other analogous affections, such as nervous headache, violent megrim, satyriasis, &c.

The following are the different forms in which he prescribes this remedy:—

Pills.—Valerianate of zinc ..... 9 grs.
Gum-tragacanth ..... 30 grs.

Make into 12 pills, one to be taken in the morning and one in the evening.

Powder.—Pulverized valerianate of zinc.... 9 grs.
... sugar ..... 45 grs.

Mix, and divide into 24 packets, of which from 1 to 4 should be given daily according to circumstances.

Draught.—Distilled water ..... 5 drms. 20 drops.
Valerianate of zinc .. $1\frac{1}{2}$ gr.
Simple syrup..... 1 oz.

A spoonful every half hour.—*Journ. de Pharm.* for August 1844.

On a new Cement for the Teeth. By Dr. Ostermeyer.

By imitating as much as possible the principles constituting the enamel of teeth, Dr. Ostermeyer has succeeded in obtaining a combination which, at first soft, gradually hardens when it has been introduced into the cavity of carious teeth; so that hollow teeth thus filled are rendered as efficient for the purposes of mastication as sound teeth.

This compound is prepared in the following manner:—13 parts of pure and finely powdered caustic lime are rapidly mixed with 12 parts of anhydrous phosphoric acid; a sufficient quantity of this powder, which has become moist during the mixing, is introduced into the cavity of the tooth, previously dried by means of blotting-paper; it is then pressed and modelled on the surface.

The mixed powder is gradually changed into phosphate of lime. As soon as it returns to the dry state, the greater proportion of the phosphoric acid has already entered into combination with the lime,

and if not applied previous to this, it is no longer fit, and should be rejected as useless. The time during which this mixture can be applied is at the utmost from one to two minutes.

Experience has already shown that this cement becomes very solid and supports perfectly the efforts of mastication; it now remains to be seen whether the duration of the compound will answer to the other advantages it presents.

On a new Method of preparing Iodide of Potassium.
By R. Phillips, Jun.

In examining six samples of iodide of potassium, procured at different chemists, the author found that No. 1 was strongly alkaline, and contained water, iodate of potash and chloride of potassium or sodium; No. 2 resembled No. 1, except that it contained a larger quantity of iodate; No. 3 was slightly alkaline, contained no water, but a trace of an iodate and chloride; No. 4 resembled No. 1; No. 5 was almost pure, containing only a trace of iodate and water; No. 6 resembled No. 1. The author proposes the decomposition of the iodide with nitrate of silver, washing the precipitate with distilled water, and then digestion in strong solution of ammonia, as a readier and better process for detecting the adulteration with a chloride than the method in general use. If the filtered ammoniacal solution, acidified with nitric acid, give a white precipitate, it is chloride of silver, and denotes the presence of a chloride of potassium and sodium. In testing for iodate of potash, the solution of the iodide in cold distilled water is to be acidulated with tartaric acid, and a solution of starch added; if the mixture does not become of a dark colour, no iodate is present.

The author's process consists in decomposing the iodate of potash formed by the action of iodine on potash by protoxide of iron. The usual method, viz. fusion of the iodide so as to decompose the iodate, is objectionable, because a heat which is sufficient to decompose the iodate renders the iodide volatile. The protoxide of iron is easily prepared by precipitation with the alkalies from the protosulphate of iron. The precipitate must be washed by decantation, until chloride of barium causes no precipitate in the water. Peroxide of iron being a sesquioxide, it is necessary, in order that the whole of the iodate may be decomposed, that for every atom of carbonate of potash used, there should be present 2 atoms of protoxide of iron. The quantities therefore should be 2 atoms or 280 parts of protosulphate of iron, which are to yield 2 atoms of protoxide, 1 atom or 125 parts of iodine, and 1 atom or 83·5 parts of carbonate of potash. On account, however, of the liability of the protoxide of iron to become peroxidized, it is better to take rather more of the protosulphate.

The protoxide, when washed, is to be mixed with the iodine and carbonate of potash, half a pint of water being used to an ounce of iodine. The mixture is at first to be gradually heated, and then boiled for half an hour. The solution afterwards ought to be exactly

neutral to slightly reddened litmus-paper; if iodine be in excess, more carbonate of potash must be added; if, on the contrary, it is alkaline, more protoxide of iron and iodine. The sesquioxide of iron remaining, after being well washed, may be heated red-hot for a few minutes; a beautifully pure preparation remains, which on account of its easy solubility in hydrochloric acid might be advantageously used in the preparation of the *Tr. Ferri Muriatis.*—*Pharm. Journ.* for August.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Acetic Acid. By M. Melsens.

According to Mr. Thompson, there exists an acid acetate of potash containing 6 equiv. of water of crystallization. M. Detmer* has confirmed the formation of an acid acetate of potash, when a current of chlorine is passed through a solution of neutral acetate. He does not give the analysis of this salt, his experiments being made with a different object in view.

In 1839, I obtained and analysed an acid acetate of a composition different from that attributed to it by Mr. Thompson. I did not endeavour to reproduce the salt of the English chemist, when I found that, on determining the potassium from three or four successive crystallizations, I always obtained about 25 per cent. of this body, whilst a salt with 6 equivalents of water would give less than 20 per cent.

The biacetate of potash, such as I obtain by supersaturating acetate of potash with distilled acetic acid, evaporating and allowing it to crystallize, appears to me to deserve the attention of chemists on more than one account. It varies in appearance according to the state of concentration, the degree of acidity, and the temperature at which it is deposited. It is obtained in the form of prismatic needles or of lamellæ, which on being dried between folds of blotting-paper have a pearly lustre. When it is slowly crystallized, it separates in the form of long flattened prisms, which, according to some measurements made by M. de la Provostaye, seem to belong to the right rectangular prismatic system. These crystals are very flexible; they may be rolled up; they cleave in every direction. They liquefy when exposed to the air, but are much less deliquescent than the crystals of the neutral acetate or of the effloresced neutral acetate. They dissolve better in hot anhydrous alcohol than in cold; a concentrated solution solidifies nearly to a mass on cooling. The alcoholic vapours are acid when the salt is heated in this medium. When it has been dried in a dry atmosphere, it may be heated to 248° Fahr. *in vacuo*, without losing more than two or three thousandths

* Philosophical Magazine for June 1841.

of its weight by this operation. At about 298° Fahr. it melts and loses some traces of acid, without doubt by the intervention of the hygroscopic water of the atmosphere. On cooling, it becomes a crystalline mass. Its boiling point is about 392°, but in proportion as it loses crystallizable acetic acid, its boiling point rises to 572°, at about which temperature the neutral acetate which remains in the retort melts and is decomposed.

This salt is represented by the formula—

$$C^8 \frac{H^7}{K} O^8$$

$$\text{or } C^4 \frac{H^3}{K} O^4 + C^4 H^4 O^4.$$

On analysis it afforded—

	I.	II.	Equiv.		Calculated.
Carbon	29·6	29·9	8 =	48·00	30·3
Hydrogen	4·3	4·4	7	7·00	4·4
Potassium	24·8	25·2	1	39·25	24·8
Oxygen			8	64·00	64·0
				158·25	

The formula which I have given is confirmed by the decomposition which the salt undergoes by heat. 1·056 grms. of the crude acid, obtained by decomposing the biacetate, and collected between 482° and 536°, gave on analysis—

	Found.	Equiv.		Calculated.
Carbon	39·9	4 =	24	40·0
Hydrogen	6·7	4	4	6·7
Oxygen		4	32	53·3

This means of procuring acetic acid chemically pure will doubtless be preferred in laboratories to the old method; it furnishes about the third in weight of acetic acid of the biacetate of potash employed, and might, with some modifications, which render the preparation of the biacetate unnecessary, become a manufacturing process.

In fact, when an excess of acetic acid, which is not too dilute, is distilled over the neutral acetate of potash, one portion of the acid combines with the potash, whilst the other, having become more aqueous, passes over. But in proportion as the temperature is increased, the distilled acid becomes stronger, and at last pure crystallizable acid is obtained, if care be taken not to go beyond 572°, about which temperature the acid that distils over acquires at first a faint rose-colour, and afterwards smells of empyreuma and of acetone, which it is however easy to avoid.

The following is the analysis of an acid thus obtained. I contented myself with purifying it by simple distillation, rejecting the first and last portions:—

1·984 gr. of acid, boiling at about 246°, gave—
1·191 gr. of water, whence ..... H = 6·7
2·880 grs. of carbonic acid, whence ..... C = 39·6

These numbers correspond closely to the formula for the acid with 1 atom of water.

These facts will probably one day be taken advantage of. In fact, in a manufactory of pyroligneous acid, sending out acids of different degrees of concentration, an apparatus arranged for the distillation of acetic acid over acetate of potash might furnish them without this salt ever being destroyed. By means of previously-ascertained proportions of dilute acid and acetate of potash, suited for the production of acid of the required strength, different hydrates might be obtained, and about one-third (37·09 per cent.) in weight of crystallizable acid of the neutral acetate of potash employed.

Very probably the consumption of monohydrated acetic acid would increase were its actual price lowered, as it constitutes a valuable solvent for removing resins, wax and fatty matters.

The acid, however, should not be diluted beyond a certain limit, which might form the starting-point in a manufactory on this principle. It is based on the following experiment:—

When a current of steam is passed into the biacetate, the acetic acid, which displaces the water of the neutral acetate of potash, is displaced in its turn by the water when this is in excess.—*Comptes Rendus*, Sept. 23, 1844.

PATENTS.

Patent granted to Thomas Drayton, Brighton, Sussex, *for Improvements in Coating Glass with Silver, for Looking-glasses and other Uses.*

A MODE of silvering glass, for looking-glasses and other uses, without the employment of quicksilver, constitutes the subject of this patent. It consists in depositing silver, from a solution, upon glass, by deoxidizing the oxide of silver in solution, in such a manner that the precipitate will adhere to the glass, without the latter having been coated with metallic or other substances.

A mixture is first made of 1 oz. of coarsely pulverized nitrate of silver, $\frac{1}{2}$ an oz. of spirits of hartshorn and 2 oz. of water; which, after standing for twenty-four hours, is filtered (the deposit upon the filter, which is silver, being preserved), and an addition is made thereto of 3 oz. of spirit (by preference, spirit of wine) at 60° above proof, or naphtha; from 20 to 30 drops of oil of cassia are then added; and, after remaining for about six hours longer, the solution is ready for use. The glass to be silvered with this solution must have a clean and polished surface; it is to be placed in a horizontal position, and a wall of putty, or other suitable material, formed around it; so that the solution may cover the surface of the glass to the depth of from an eighth to a quarter of an inch. After the solution has been poured on the glass, from 6 to 12 drops of a mix-

ture of oil of cloves and spirit of wine (in the proportion of 1 part by measure of oil of cloves to 3 of spirit of wine) are dropped into it at different places; or the diluted oil of cloves may be mixed with the solution before it is poured upon the glass; the more oil of cloves used, the more rapid will be the deposition of the silver; but the patentee prefers that it should occupy about two hours. When the required deposit has been obtained, the solution is poured off; and as soon as the silver on the glass is perfectly dry, it is varnished with a composition formed by melting together equal quantities of bees' wax and tallow. The solution, after being poured off, is allowed to stand for three or four days in a close vessel, as it still contains silver, and may be again employed after filtration, and the addition of a sufficient quantity of fresh ingredients to supply the place of those which have been used. The patentee states that, by experiment, he has ascertained that about 18 grs. of nitrate of silver are used for each square foot of glass; but the quantity of spirit varies somewhat, as its evaporation depends upon the temperature of the atmosphere and the duration of the process.

If the glass be placed in an inclined, or even a vertical position, and the surface covered over, leaving a narrow space for the solution between the surface of the glass and the cover, which fits close, then, by using spirit with water in the mixture, the object will be accomplished. By the addition of a small quantity of oil of caraway or thyme, the colour of the silver may be varied. The oil of cassia, purchased of different manufacturers, varies in quality; therefore if, on being mixed with the solution, it should become flaky, the solution must be filtered previous to use.

The patentee does not confine himself to the precise details herein described, provided the peculiar character of the invention be retained, whereby silver is deposited on to glass from a solution of that metal, by deoxidation, in such a manner as to cause the silver to adhere to glass without any previous coating of the latter.—Sealed Nov. 25, 1843.

Patent granted to William Godfrey Kneller, Wimbledon, Surrey, *for Improvements in the Preparation of Zinc, and in Combinations of Zinc with other Metallic Bodies.*

This invention consists in purifying zinc by the employment of melted lead, and, by the use of such purified zinc, forming combinations with copper, and other metals, of a more useful character than can be obtained with zinc in its ordinary state.

The zinc and lead are melted together (by preference, in equal quantities), and, after being well stirred, the impurities that rise to the surface are skimmed off; powdered charcoal is then thrown on the surface, to prevent oxidation, and the metals remain in a melted state for about 3 hours, when the lead will have descended to the bottom of the vessel, leaving the purified zinc floating at the top; the charcoal and other impurities are then removed from the surface by skimming, and the zinc is drawn off through a pipe in the side of

the pot. The patentee generally uses a melting pot similar to those used for melting 14 cwt. of lead, but rather deeper, and puts into it 7 cwt. of zinc and 7 cwt. of lead.

When it is desired to combine a small portion of the zinc with the lead, so as to form an alloy, the metals are not allowed to stand for 3 hours, as above; but, after an hour has elapsed, the greater part of the zinc is drawn off, leaving a thickness of about an inch upon the lead, which, as it cakes in cooling, is skimmed off, and the lead remaining will be found to be combined with zinc. The zinc that has been drawn off contains a certain quantity of lead, which may be separated by keeping it in a heated state.

For making alloys with copper and other metals, zinc is used from which the lead has been completely separated.—Sealed March 14, 1844.

Patent granted to Peter Ward, West Bromwich, Warwick, *for an Improvement in combining Matters for Washing and Cleansing.*

The object of this invention is to combine glue or gelatine and mucilage with soda or potash, in such a manner as to render the compound suitable for washing and cleansing purposes.

The mode of forming the compound, preferred by the patentee, is as follows:—By means of edge-stones, or other machinery, a quantity of soda ash of commerce is ground with a solution of glue (formed by dissolving 1 cwt. of glue in 45 gallons of water) into a thick paste or dough, which is spread on the floor of a room to dry; after 4 hours have elapsed it is turned with a shovel, and then allowed to remain for 10 hours longer, when it is again turned, and left for about 10 hours more, or until it is quite dry, after which it is passed through a sieve of 4 meshes to the inch. Although soda ash is preferred by the patentee, soda in other states may be used; and likewise potash may be substituted for the soda.

The above matters may also be obtained in a combined state, by dissolving the glue and alkali in water.

When mucilage is to be used, instead of, or with glue or gelatine, a thick jelly is made from linseed or linseed oil-cake, and, after the insoluble matters have been strained off, it is mixed and ground with the alkali, in the same manner as the dissolved glue or gelatine. —Sealed March 4, 1844.

THE CHEMICAL GAZETTE.

No. L.—November 15, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Atomic Weight of Iron, according to the Researches of Svanberg, Norlin, Berzelius, Erdmann *and* Marchand.

Some experiments lately published by Wackenroder pointed to the fact that the peroxide of iron must contain less oxygen than is found according to the atomic weight 339·2 for iron. This statement induced Berzelius to engage Svanberg to undertake a fresh examination of the atomic weight of iron, who has executed it in company with M. Norlin.

Their experiments are of two kinds,—1st, oxidation of the iron with nitric acid, drying the nitrate of iron, and ignition of the residue; 2nd, reduction of peroxide of iron by means of hydrogen gas, which has been passed through a solution of oxide of lead in potash, and then dried by chloride of calcium. Seven experiments were made according to each of these methods.

In the experiments of oxidation they thought they observed that when they were performed in platinum crucibles, the catalytic influence of the metal during ignition produced a slight loss of oxygen in the peroxide of iron at those places where the oxide was in immediate contact with the platinum; consequently only those experiments have been regarded as correct which were executed in glass vessels. The seven experiments made in this manner gave for the atomic weight of iron as minimum 348·72, as maximum 349·523.

The experiments of reduction were effected with the necessary measures of precaution, in order that the iron should be perfectly reduced, as well as that no condensation of gas could take place in the reduced metal. These experiments gave for the atomic weight of iron, as minimum 350·093, as maximum 350·828. The mean of all fourteen experiments gives the atomic weight of iron *in vacuo* at 350·809; according to which the protoxide of iron contains 22·2436 per cent., the peroxide 30·0114 per cent. oxygen.

This result differs nearly by 10 units from the atomic weight hitherto admitted, which induced Berzelius himself to test the same by experiments. For these experiments he employed some iron which had been mixed in small fragments with non-metalliferous glass and protoxide of iron, and then fused with coke in a crucible

of fire-proof clay, so that it was freed as much as possible from carbon and silica by the influence of the oxide of iron in fusing. This iron was dissolved in nitric acid, the solution evaporated to dryness in a platinum crucible, and the residue ignited in the closed crucible. One experiment performed in this manner gave as the atomic weight of iron 350·27, the other 350·369. These numbers are intermediate between the minimum and maximum found by Svanberg and Norlin, and consequently confirm their result.

MM. Erdmann and Marchand have likewise instituted some experiments on the same subject; they made use of a very finely-divided oxide, which they procured by igniting the oxalate of the protoxide of iron in a current of air or of oxygen. The first series of experiments were made with precipitated oxalate of the protoxide, obtained by mixing pure oxalic acid with protosulphate of iron. The latter salt was procured by dissolving pure sulphuret of iron, prepared from piano-forte wires and pure sulphur, in distilled sulphuric acid; it was recrystallized several times. so that no doubt could be entertained as to its purity. The precipitated salt was washed with boiling water, dried and ignited; it was converted, by gentle heat and exposure to the air, entirely into peroxide of iron; not a trace of protoxide had remained in it after it had been frequently ignited, with stirring, in shallow platinum vessels. Experiment 5 of the first series was made with a peroxide which had been thus prepared; the others were subsequently moistened with nitric acid and ignited; no essential difference, however, was apparent, so that this measure of precaution did not seem to be requisite.

For the second series of experiments an oxide prepared from the protoxalate of iron was employed, which had been obtained by the reduction of the binoxalate of the peroxide of iron in the light of the sun. The pure, perfectly-washed protosalt was ignited, moistened with nitric acid, and again ignited, until after several ignitions no difference in weight was evident in the platinum crucible. The ignition cannot be effected in a furnace, since in the present instance, as with the oxide of copper, the peroxide is partially reduced to protoxide, as is likewise the case on fusing ferriferous silicates, for instance garnets. The green colour which they acquire after fusion in a furnace is owing to that circumstance, which also explains the loss in weight they undergo in this operation. On igniting the pulverized mineral exposed to the air, the red colour again makes its appearance, and at the same time an increase in weight is perceptible.

After the reduction of the oxide, it is difficult, on expelling the hydrogen gas by atmospheric air, to protect the metal obtained from partial oxidation, although it had been exposed to a very high temperature during the reduction. Thus, for instance, on employing 29·2576 grms. peroxide of iron for reduction, the weight of the iron at the first weighing was 20·521; but after being ignited again in hydrogen, and the expulsion of this gas by means of air, the residue weighed 20·551; the oxidation therefore had increased during the passage of the atmospheric air. For this reason, and at the same time to avoid the somewhat uncertain calculation for the reduction to

vacuum, the authors employed the same method they have described for the reduction of the oxide of copper by oxygen, viz. weighing *in vacuo* the tube in which the reduction was effected emptied of air, and determining the weight of the peroxide employed, as well as that of the iron obtained, likewise *in vacuo*.

The course pursued in the reduction was identical with that which the authors have described in the reduction of the oxide of copper*; it was generally effected over spirit-lamps, and only once in a charcoal fire. The hydrogen was consecutively passed through a solution of oxide of lead in potash, solution of corrosive sublimate, concentrated sulphuric acid, solution of sulphate of silver, and lastly over dry caustic potash. It was perfectly free from smell, and burnt with an imperceptible flame. The following numbers were obtained in the several experiments:—

1st series.	2nd series.
70·013 per cent iron.	70·044 per cent. iron.
69·962 ...	70·015 ...
69·979 ...	70·055 ...
70·030 ...	
69·977 ...	

The number 69·962, the lowest of all, would give as atomic weight 349·3; the number 70·044, the highest, gives 350·7; the mean of all the experiments gives 70·009 per cent. iron and 29·991 per cent. oxygen; consequently the atomic weight of iron is 350·1, or 28·008, H = 1.

The mean of all the series of experiments gives as the atomic weight of iron almost exactly the number 350, or 28 times that of the equiv. of hydrogen.—*Journ. für Prakt. Chem.*, xxxiii. p. 1.

On a new Acid in the Urine of Man. *By* W. Heintz.

Liebig assumes as certain, that as lactic acid is not destroyed by putrefaction, it cannot be altered in putrefied urine. The former is generally admitted, but whether certain causes do not prevail during the putrefaction of the urine which might cause the destruction of the lactic acid seemed still to require experimental proof.

About 50 lbs. of fresh urine, obtained from several young healthy men, were first evaporated over a free fire, and then in the water-bath; the extract obtained exhausted with alcohol, to which a sufficient quantity of dilute sulphuric acid had been added. The acid solution was saturated with oxide of lead, the precipitate filtered, the liquid much evaporated, and the urea contained in this concentrated solution precipitated with pure oxalic acid. A considerable quantity of oxalate of urea was obtained, which, after washing with water and recrystallization, separated perfectly white and in large crystals. The liquid, separated by pressure from the urea, from which it was now almost free, was evaporated to dryness, extracted with alcohol, and effloresced oxalic acid added to the solution to

* See present volume of this Journal, p. 399.

remove the soda. The oxalate of soda was separated by filtration, the filtered solution saturated with oxide of lead, and then precipitated with basic acetate of lead. The lead was removed from the filtered liquid by sulphuretted hydrogen, filtered, and the solution, concentrated over the water-bath, boiled with hydrate of barytes, when a considerable disengagement of ammonia resulted. The salt of barytes obtained in solution was then decomposed with sulphate of zinc, in such a manner that only a slight excess of this latter remained in the solution. It was then evaporated to a small volume, when some delicate microscopic crystals separated, which were at first taken for lactate of zinc, but on examination under the microscope they soon proved to be distinct. The lactate of zinc, for instance, forms needles with acute dihedral summits, while the crystals of the zinc salt obtained from the urine have truncated terminal surfaces. To ascertain more precisely the nature of the acid combined with the oxide of zinc in this salt, the crystals were separated as carefully as possible from the mother-ley, pressed between blotting-paper, dissolved in a large quantity of boiling water, in which they were but sparingly soluble, and allowed to crystallize by cooling. The mother-ley afforded more crystals on further evaporation. They were again separated from adhering liquid by pressure.

The zinc salt thus obtained had a faint greenish-yellow tint, and was therefore probably not quite pure, although its solution was perfectly colourless. The acid was isolated from this salt by means of sulphuretted hydrogen; after separation of the sulphuret of zinc the solution was entirely free from zinc. The solution, which had a strong acid reaction, was freed by boiling from the excess of sulphuretted hydrogen, and evaporated in the water-bath. When the liquid had become sufficiently concentrated, the acid separated in prismatic crystals, which appeared to form quadrilateral rectangular columns and tables. It is easily soluble in water, and separates on evaporation in crystals; the solution has a strong acid taste, and reddens litmus-paper. It likewise dissolves in alcohol, but not quite so easily as in water; æther dissolves scarcely a trace of it. Heated on platinum foil, it melts, becoming brown, and leaves behind a coal, which is difficult of combustion, but which disappears entirely by stronger heat.

From the mode of preparation it is evident that the acid forms with oxide of zinc a very sparingly-soluble salt, which separates in microscopic crystals. When the acid is supersaturated with ammonia, and the solution evaporated in the water-bath, so much ammonia escapes that it again becomes acid; if it be evaporated to dryness, so that all the ammonia that could escape at this temperature is expelled, and caustic potash be added to the mass, a considerable quantity of ammonia is given off; therefore it appears that this acid, like so many organic acids, forms acid salts. The ammonia salt obtained in this manner is somewhat more difficult of solution in water than the acid itself. When the acid is accurately neutralized with potash, it forms an easily-soluble salt, the solution of which affords no precipitate with sulphate of copper. The oxide of copper is not

thrown down from this mixture by an excess of potash, but the colour of the solution becomes somewhat darker. Acetate of lead produced a slight turbidness, which most probably arose from a small quantity of some impurity. No precipitate was obtained with nitrate of silver, and the mixture, after having been rendered ammoniacal, was not altered by boiling. A solution of perchloride of iron, rendered neutral by ammonia, produced no precipitate. It differs, therefore, likewise, by this reaction from hippuric acid. Solutions of alum, chloride of barium and chloride of soda, afforded no precipitate with it, the latter not even when they had been previously rendered ammoniacal.

The author has not yet been able to ascertain the composition of this acid, from the quantity which he obtained from 50 lbs. of urine being very small. It amounted to about half a gramme; at the same time it was not perfectly white. But it was easy to prove that it contained nitrogen in considerable quantity.—Poggendorff's *Annalen*, lxii. p. 602.

On the Action which Iodine exercises on some Salts, and the resulting Products. By M. Filhol.

Several years ago M. Berthemot obtained a compound of iodine and lead of a beautiful blue colour. This compound was subsequently noticed by M. Denot, and has been recently studied by M. Durand*.

To establish its chemical composition, I first studied that of the solutions which produce it. The first part of my researches contains the investigation of the action which iodine exercises on the carbonates. The result of my experiments proves that iodine acting in a cold state on the alkaline carbonates, forms bicarbonate of the base, some iodide and iodate.

In studying the action which a solution of biniodide of potassium exerts on a solution of acetate of lead, I have succeeded in producing a precipitate of a very unstable violet-red; this compound, heated to 230° Fahr., loses 26·66 per cent., or 1 equiv. of iodine, and leaves a residue constituted of $I\,Pb + PbO$. If care is taken not to exceed 230°, the residue is of a beautiful green colour; but if the temperature is increased to 266° or 286°, it loses its green colour and becomes of a pale yellow, without parting with the slightest trace of iodine.

The composition of this red powder is such, that it may be considered as formed of biniodide of lead combined with oxide of lead $(I^2 + Pb) + PbO$, or as formed of $I\,Pb + I\,PbO$.

This powder is decomposed when treated with acetic acid in excess; some iodine is set free, the oxide of lead combines with the acetic acid, and a new iodide of lead, formed of $2\,I\,Pb + PbO$, is left.

I have shown, in the latter part of my researches, that this red powder constitutes one of the elements of the blue compound of

* See *Chem. Gaz.* vol. i. p. 87.

which I have already spoken, and that to produce the latter it suffices to bring the red powder still moist into contact with some carbonate of lead *in statu nascenti*, or better still, to employ a solution which produces them both at the same time. The blue powder constitutes a new kind of compound, and I propose to give it the name of *iodocarbonate of lead.*

It is obtained in a very beautiful form by using a solution consisting of 1 proportion of biniodide of potassium and 4 of carbonate of potash, to precipitate a solution of acetate of lead.

I have also described the means of transforming the ordinary yellow iodide of lead into a beautiful blue powder. The analysis of a fine sample of this blue compound has led me to assign to it the formula $I\,Pb + I\,PbO + 4(C^2\,O^2\,PbO)$.—*Comptes Rendus*, Oct. 14, 1844.

On a new Combination of Sulphur with Chlorine and Oxygen. *By* M. E. Millon.

While endeavouring to produce a higher chloride of sulphur than that which has hitherto been obtained, I had frequently remarked the formation of a crystalline product, which I supposed to consist solely of sulphur and chlorine. But on reproducing this combination several times, I discovered that it was formed only in proportion as the chlorine was slightly moist and in great excess. From this moment I suspected the presence of oxygen in it. By a particular method of preparation I succeeded in obtaining this product in very considerable quantity. I then submitted it to analysis, and found in it, besides a large proportion of oxygen, certain properties which are of the highest interest in relation to the isomeric transformation of mineral compounds.

The new compound under consideration is immediately obtained by conveying a few drops of chloride of sulphur into an imperfectly dried flask containing some chlorine moistened by its passage through a washing flask. Too large a quantity of moisture would instantly destroy the compound or arrest its production; but under the circumstances mentioned the sides of the flask soon become covered with colourless transparent crystals. It is, however, impossible to remove the compound thus distributed in thin layers, without its being instantly destroyed by the moist air. To prepare it in quantity sufficient for analysis, the following process is adopted:—

A flask is filled with 4 or 5 quarts of moist chlorine; then from 20 to 30 grms. of chloride of sulphur, already saturated with chlorine, are introduced, and lastly 2 or 3 grms. of water. It is agitated, and the flask surrounded with a refrigerating mixture of ice and salt for 4 or 5 hours. A great disengagement of hydrochloric acid takes place. The flask is again filled with moist chlorine, and placed in the refrigerating mixture. These operations are renewed until the chloride of sulphur solidifies for the greater part to a crystalline mass, which floats in the midst of an excess of chloride of sulphur. This formation of crystals, which are sometimes acicular, sometimes

wide rhomboidal laminæ, is generally preceded by the production of a yellowish liquid, heavier than the chloride of sulphur, from which it separates in the manner of an oil.

It is extremely difficult to separate the crystals thus obtained from adherent chloride of sulphur, which can only be effected by passing a current of chlorine, dried over sulphuric acid, into the flask during 10 or 12 hours. While the dried chlorine is being passed through the flask, the crystals are sublimed by means of incandescent charcoal from one side of the vessel to the other; the crystals, nevertheless, always retain one or two hundredths of chloride of sulphur, which varies, as shown by analysis, in proportion to the time during which the current of chlorine was passed.

It is almost impossible to analyse these crystals immediately after their production; they are, in fact, destroyed with great violence on being brought into contact with water, alcohol or weak acids, being projected in every direction. To determine their composition, I took advantage of the following very interesting property:—When the crystals have been freed as much as possible from the chloride of sulphur, they are dropped into a very dry glass tube, closed at one of its extremities, and whose open extremity is quickly sealed over a lamp; after 2 or 3 months they become soft, pasty and moist, and after 7 or 8 months they are converted into an extremely fluid liquid, and of a faint yellowish colour, which however is almost imperceptible when the current of chlorine had been continued for some length of time. No absorption takes place, no decomposition of the compound, which it is impossible to solidify again by the application of cold of $-1°$. It is therefore an isomeric transformation, which is not only evidenced by the change in its physical properties, but also in its chemical properties; thus the liquid when thrown into water no longer produces the sound of red-hot iron suddenly extinguished, which was caused by the crystals. It can very well be treated with weak acids, alcohol, and with water, at the bottom of which it is quickly deposited in the form of an oil, which at length completely changes into sulphuric, sulphurous and hydrochloric acids.

This transformation is quite in accordance with the analysis, which leads us to represent it as a combination of sulphur, chlorine and oxygen in the proportions $S^2 O^3, Cl^2$.

It is a different compound from the combination discovered by M. Regnault, SO^2, Cl, and from the liquid analysed by M. Henry Rose, and represented by $S^2 O^5, Cl$.

The analysis of the combination above described, and which may be designated by the name of hypochlorosulphuric, offers no difficulty in the liquid modification; it suffices to fill a weighed phial with it, which is broken in a flask containing some fuming nitric acid. The vivacity of the reaction is moderated by cooling the flask; it is then easy to determine the sulphur in the state of sulphate of barytes, and the chlorine in the state of chloride of silver.

The analyses agree perfectly with each other.—*Comptes Rendus* for Oct. 1844.

Effects of Nascent Oxygen on certain Organic Alkalies.
By Eugene Marchand.

When excess of peroxide of lead is boiled in a solution of sulphate of cinchonine, quinine, morphine, narcotine, strychnine or brucine, and sulphuric acid is added drop by drop, until a portion of the filtered liquor, tested with ammonia, potash, or its carbonate, ceases to become turbid, there occurs a brisk effervescence of carbonic acid gas, and the liquor becomes of a deeper colour; if the operation be then stopped and any free acid which may exist in it be saturated with litharge, the solution evaporated to dryness, and the mass be treated with distilled water, and the solution obtained with sulphuretted hydrogen, which sometimes precipitates a little sulphuret of lead, and lastly the filtered liquor be evaporated to dryness, very distinct colouring matters are procured from each organic alkali; these colouring substances are the following:—

Cinchonetine; this is obtained by the process above described from cinchonine; it is an uncrystallizable amorphous substance, of a very deep violet colour when viewed in mass, and yellowish red in very thin layers. It is deliquescent, and has a bitter taste. When attempts are made to incinerate it, it fuses, yields white vapours as cinchonine does, the odour of which is not at all ammoniacal; it inflames and burns with a sooty flame, and leaves a charcoal which it is very difficult to incinerate.

Cinchonetine dissolves more readily in boiling than in cold water; its best solvent is alcohol; æther does not act upon it; concentrated sulphuric acid dissolves it very easily and becomes of a red colour, but without apparently altering it; if this solution be treated with water, it assumes a yellow tint, but is not rendered turbid.

The aqueous solution of cinchonetine, which is of a red colour, is not rendered turbid either by ammonia or potash, but they change the colour first to purple and afterwards to fawn colour, and acids do not restore the original tint; subacetate of lead occasions a violet precipitate, which soon subsides; chlorine instantly destroys the colour. By the combined action of sulphuric acid and peroxide of lead, cinchonetine may be converted into fresh colourless compounds, and acetic acid appears to be one of them.

Quinine.—The result of the action of nascent oxygen upon this alkaloid is a complex substance, upon which heat acts as it does upon cinchonetine; and it may be separated into at least two distinct principles, *quinetine* and *modified quinetine*. The former of these remains when the complex colouring matter is treated with water, in which it is insoluble; it dissolves, however, in alcohol, and imparts a violet colour to it; the modified quinetine, on the contrary, is soluble in water, and the solution has a blood-red colour.

Modified Quinetine is an amorphous mass, of a red colour, has a bitter taste, and is soluble in water, alcohol and æther; when the aqueous solution is boiled, in order to evaporate it to dryness, it is decomposed, and deposits a black powder which is insoluble in alcohol and æther.

Potash and ammonia decolorize the aqueous solution of this substance, which from red becomes of a dirty yellow colour; it is not, however, altered, as cinchonetine is, for by saturating the alkali with sulphuric acid the original may always be restored. Modified quinetine dissolves in concentrated sulphuric and nitric acids, and imparts its colour to them.

Quinetine.—By the spontaneous evaporation of the alcoholic solution, this substance may be obtained for the most part crystallized. It is insoluble in water, but dissolves extremely well in alcohol, æther, and water acidulated with sulphuric acid; to the first two solvents it gives a violet colour, and to the last a red one. Although this substance is insoluble in water, its alcoholic solution is not rendered turbid by the addition of water.

Potash and ammonia act upon it in the same way as upon the modified quinetine.

The concentrated acids dissolve quinetine and acquire a red colour; it probably passes to the state of modified quinetine.

By repeated solutions and evaporations, quinetine may be rendered soluble in water, and it then appears to possess all the properties of modified quinetine.

Morphine.—Morphetine amorphous, brown and slightly bitter, little soluble in alcohol, but imparts a yellow colour to it; on the other hand it is very soluble in distilled water, to which it gives a reddish-yellow colour, and the property of reddening litmus paper. Sulphuric and nitric acids turn the colour of this solution to pale yellow, whereas it becomes deeper by the caustic alkalies. Subacetate of lead does not alter or precipitate this solution; concentrated sulphuric acid dissolves morphetine with difficulty, but nitric acid dissolves it readily and acquires a yellow colour. Morphetine, when submitted to the action of peroxide of lead till effervescence ceases, is converted into a yellow deliquescent uncrystallizable substance, possessing acid properties.

Narcotine.—Narcoteine is an amorphous, uncrystallizable mass of a brown colour and very bitter taste; it is very slightly soluble in æther, but readily so in water and alcohol; it is soluble in concentrated nitric acid, and renders it yellow; it also dissolves, and with great facility, in concentrated sulphuric acid, rendering it of a magnificent red colour, which becomes yellow on the addition of water.

The aqueous solution of narcoteine is of a yellow colour; when either ammonia or potash is added to it, the colour becomes rather brighter, and reddish-brown. Subacetate of lead does not alter either its colour or transparency.

When narcoteine is subjected to the action of nascent oxygen, until effervescence ceases, it is slightly decolorized, and is converted into a new substance, opianic acid, previously obtained by MM. Liebig and Wœhler in their experiments on the oxidizement of narcotine.

Strychnine.—This treated like the preceding yields a pulverulent mass of a brownish yellow colour, very slightly soluble in boiling water, but imparts to it a dirty yellow colour and a bitter taste; it is

very slightly soluble in alcohol, but soluble in æther, and also in boiling water acidulated with sulphuric acid; and from this the greater part precipitates on cooling.

Potash is the best solvent of this substance; the solution has a brown colour, and if only the exact quantity of potash required for solution be employed, the solution does not act on syrup of violets. When sulphuric acid is added to the solution, so as to give it an acid reaction, it becomes turbid, and deposits a yellowish flocky precipitate. The alkaline solution, when perfectly neutralized, does not act upon cupreous or ferruginous salts, but it precipitates the salts of lead and silver.

This substance is worthy of the attention of chemists; the remarkable manner in which it acts with potash, appearing to saturate it perfectly, will perhaps lead to its being considered as a new acid.

Brucine.—By the action of nascent oxygen on this alkaloid two colouring matters are obtained; one which is soluble in boiling alcohol, to which it gives a yellowish-red colour; this will be described as A; the other, B, is insoluble in boiling alcohol, but when diluted with an equal volume of water it is then dissolved readily; the resulting solution has a fine red colour.

A. This is a brown, uncrystallizable substance; it has a very bitter taste, and is very little soluble in æther, but is dissolved by boiling alcohol; distilled water dissolves it and acquires a yellowish-red colour; it is soluble in concentrated nitric acid, and produces as fine a colour as brucine; sulphuric acid also dissolves it, but more slowly; and the solution has also a very fine red colour; hydrochloric and acetic acids and potash likewise dissolve it very well, but the solutions have a yellow colour.

B. This substance, like the preceding, is uncrystallizable; its taste is bitter, and when in mass it is black, but in thin portions its colour is red; it is insoluble in æther and in boiling alcohol, but dissolves very well in the latter when diluted with water; it is soluble in distilled water, to which it imparts a fine wine-red colour, which acids brighten slightly, whilst potash renders it brownish and subacetate of lead yellow.

The concentrated sulphuric and nitric acids dissolve this substance, and so does potash, the solutions acquiring a yellowish-red colour of less or greater intensity.—*Journ. de Chim. Médicale*, July 1844.

On the Combinations of Phosphorus with Hydrogen.
By Paul Thenard.

According to the author there exist at least three phosphuretted hydrogens, a solid, a fluid and a gaseous one. The solid one, already described by Leverrier, is P^2H; it is best obtained by passing inflammable phosphuretted hydrogen gas into muriatic acid, washing the precipitate which forms in cold water, and drying it *in vacuo*.

The non-inflammable phosphuretted hydrogen is most advantageously procured by conveying phosphuret of calcium into con-

centrated muriatic acid, when the yellow solid combination separates at the same time. The inflammable gas obtained from phosphuret of calcium and water is constantly mixed with variable quantities of free hydrogen gas (which increases with the duration of the process), and its formation is never accompanied by a separation of solid phosphuretted hydrogen. The quantity of the free hydrogen is always in inverse ratio to that of the hypophosphorous acid. The inflammable gas passes into the non-inflammable modification, by exposure to light, by contact with protochloride of phosphorus, and muriatic acid, but always with separation of solid phosphuretted hydrogen. When some phosphuret of calcium, which has been mixed with phosphate of lime, is gradually added to dilute muriatic acid, it sometimes deposits a tenacious substance, which instantly takes fire on exposure to the air. The phosphuretted hydrogen gas appeared to owe its inflammability to the presence of a minute quantity of this compound.

The author passed large quantities of the inflammable phosphuretted hydrogen gas through curved tubes which were cooled to—4° Fahr. It deposited a colourless transparent liquid, which took fire immediately on exposure to the air, but was decomposed in sunlight, and likewise by muriatic acid and protochloride of phosphorus, into solid phosphuretted hydrogen and inflammable gas. It appears to become gaseous in the dark at 59° without decomposition. The smallest quantity of this liquid renders phosphuretted hydrogen gas, and even hydrogen, inflammable. This compound can only be preserved with safety in sealed tubes, which are buried in sand, owing to its explosive properties. The author has not yet analysed the fluid combination, but most probably its amount of hydrogen is intermediate between that of the solid and gaseous. As, moreover, very little of it is required to render the gas inflammable, it is not astonishing that the same results should have been obtained in the analysis of the inflammable and non-inflammable phosphuretted hydrogens.

The author prepared the phosphuret of calcium employed in the experiments by passing an excess of phosphorus over strongly heated pure carbonate of lime in a peculiar apparatus.—*Comptes Rendus*, xviii. p. 653, 1844.

On Quinon. By Prof. Wöhler*.

1. *Products of Distillation of Quinic Acid.*—Crystallized quinic acid, heated to melting in a retort, begins at about 536° to become yellow and brown with constant ebullition, arising partly from water, partly from the disengagement of a gas, which burns with a pale blue flame. On raising the temperature, a yellowish, highly crystalline sublimate makes its appearance, which gradually melts again, distils over in oily bands, and again solidifies to a pale

* The name of quinon has been proposed by Berzelius as preferable to that of quinoyle. A brief notice of these interesting products was given in our first volume, p. 400.—Ed. *Chem. Gaz.*

yellow, granular, easily fusible mass. The blackish-brown residue in the retort puffs up at last considerably.

The distillate contains, besides a tarry substance not yet examined, benzoic acid, carbolic acid, salicylous acid, benzole, and as principal constituent a new crystalline body, which will be subsequently described under the name of colourless hydroquinon.

The separation of these substances was effected by dissolving the distillate in water, removing from it the separated tar, submitting the solution to distillation, when carbolic acid, salicylous acid and benzole distilled over. From the remaining solution the benzoic acid crystallized on cooling; and finally, from the mother-ley, the colourless hydroquinon, which was purified by repeated crystallization.

2. *Quinon.*—The author observes, with respect to the preparation of this body, that the proportions by weight of quinic acid, manganese and sulphuric acid, given by Woskressensky, should be accurately observed. The quinon is readily obtained in beautiful yellow prisms, of more than an inch in length, both by sublimation as well as from its hot solution in water; it likewise solidifies after fusion to a highly crystalline mass. Its vapour violently irritates the nose and eyes, and produces a similar after-effect as iodine or chlorine.

Woskressensky has calculated the relative atomic composition of quinon as $C^3 HO$ from the results of three analyses agreeing well with each other, and appears, according to subsequent researches, to adopt the formula $C^{12} H^4 O^4$ as expressive of the absolute atomic weight; but the amount of carbon found was larger in all the analyses than that calculated according to the above formula. A fresh analysis, performed with the greatest care, gave a somewhat still higher amount than the mean of Woskressensky's analyses, recalculated according to $C = 75{\cdot}12$. The numbers obtained correspond best to the formula $C^{25} H^6 O^8$, which the author regards as the more correct expression of the composition of quinon.

3. *Colourless Hydroquinon.*—This body is the chief product of the dry distillation of quinic acid, but it can likewise be produced with the greatest ease directly from quinon, by conveying hydrogen to this. It is formed on adding hydriodic acid to a saturated solution of quinon, the liquid immediately becoming brown from the separation of iodine. On evaporation it is obtained in colourless crystals. It is further formed when telluretted hydrogen gas is passed into a solution of quinon, when pure tellurium is immediately precipitated as a gray spongy mass. The hydroquinon crystallizes from the filtered colourless liquid on evaporation.

It is best prepared by passing sulphurous acid gas into a saturated solution of quinon, in which some undissolved is suspended, until the solution is decolorized, or all the quinon dissolved. The hydroquinon crystallizes on evaporation at a gentle heat without the sulphuric acid in the ley decomposing it. Dry sulphurous acid is without action on quinon.

Hydroquinon crystallizes in colourless, transparent, very regular six-sided prisms with oblique terminal surfaces; it is void of smell,

has a sweetish taste, does not behave acid, is readily soluble in water and alcohol, and considerably more so on applying heat. It melts readily, and solidifies on cooling to a crystalline mass. Heated in a tube, it creeps along the sides, but melted between two concave plates, it sublimes in shining crystalline laminæ exactly as benzoic acid. Heated suddenly above its point of volatilization, it is partially decomposed into quinon and green hydroquinon.

The solution of hydroquinon becomes immediately coloured brown-red at the surface by ammonia, which colour rapidly diffuses itself throughout the entire liquid; on evaporation it leaves a brown humus-like mass, nor could constant compounds be produced with other bases. A solution of the peracetate of copper becomes instantly coloured of a dark saffron-yellow with the solution of hydroquinon; on the application of heat, red protoxide of copper separates, and quinon is liberated. The analysis of this body led to the formula $C^{25}\,H^{12}\,O^{8}$ for its composition; it is consequently quinon + 4 equiv. hydrogen.

4. *Green Hydroquinon.*—This beautiful substance is formed when hydrogen is eliminated from the preceding, or hydrogen in its nascent state conveyed to quinon, but not sufficient for colourless hydroquinon to be produced. In all cases where the green hydroquinon originates, it separates in a crystalline state, colouring the liquid for a moment blackish-red, and then all at once filling it with the most brilliant green prisms, which have a metallic lustre, and which frequently are more than an inch in length, even when operating with small quantities. It does not separate when the liquids acting on each other are too dilute; it is then decomposed, and the odour of quinon becomes perceptible. The crystals are collected on a filter, washed, and dried by exposure to the air, or over sulphuric acid. It is obtained most readily from the colourless hydroquinon by mixing its solution with perchloride of iron; further, when chlorine is passed into this solution, or when it is mixed with nitric acid, nitrate of silver or chromate of potash. The silver of the silver salt is precipitated in a metallic state, and green oxide of chrome from the chromate. It is likewise formed when spongy platinum or animal charcoal are moistened with the above solution and exposed to the air.

It is obtained from quinon by mixing a saturated solution with sulphurous acid, which should be added at once for the production of large crystals; however, only in such quantity that some unaltered quinon remain, as otherwise the action proceeds further—to the formation of colourless hydroquinon. The solution of quinon containing formic acid, which is obtained in the preparation of quinon, is advantageously employed for the production of the green hydroquinon; colourless hydroquinon is less easily obtained with it.

It is further formed when protochloride of tin is gradually added to a solution of quinon, or when crystals of the protosulphate of iron are placed in it, or when, after having acidulated it faintly with sulphuric acid, and rendered it conductive, zinc is immersed in it, or a galvanic current passed through it.

The most remarkable mode of formation of the green hydroquinon is by the reciprocal action of the colourless hydroquinon and quinon. When the two solutions are mixed, they combine immediately, yielding green crystals, without the formation of any other product. Alloxantine acts in the same way, and becomes converted into alloxan.

Green hydroquinon is very similar to murexide, but it surpasses it in lustre and beauty of colour; the crystals are always thin, but frequently very long. Under the microscope the more minute ones appear transparent and of a reddish-brown colour. It has an irritating taste and a faint odour of quinon; it is easily melted to a brown liquid, and sublimes partially in green laminæ, but is in part decomposed, and disengages quinon, which sublimes in yellow crystals. It is very sparingly soluble in cold, in considerable quantity in hot water, and with a brownish-red colour; on cooling it separates in crystals. If this solution be boiled it is entirely decomposed, quinon distils over, and a dark reddish-brown liquid remains, which principally contains colourless hydroquinon; but at the same time, without doubt as a secondary product of decomposition, a brown tarry substance, which separates on cooling and on the addition of water, and appears to be identical with that which is contained in the crude product of the distillation of quinic acid. Green hydroquinon is readily soluble in alcohol and æther with a yellow colour; on evaporation it is obtained crystalline and with its green metallic lustre unaltered, presenting, especially on white porcelain, a very remarkable and beautiful appearance.

It dissolves in ammonia with a dark green colour, which however immediately becomes converted, on exposure to the air, into a dark reddish-brown; it then leaves on evaporation a brown perfectly amorphous mass.

Green hydroquinon is readily dissolved by sulphurous acid, which converts it into colourless hydroquinon. It undergoes the same change under all those circumstances by which colourless hydroquinon is formed from quinon; iodurettted and telluretted hydrogen alone form an exception; these convert the quinon direct into colourless hydroquinon.

The analysis of this body afforded for its composition the formula $C^{25}\,H^{10}\,O^{8}$; therefore quinon + 2 equiv. water.

5. *Chlorhydroquinon.*—Concentrated hydrochloric acid poured over quinon turns it immediately greenish-black, and then dissolves it to a liquid, which at first is reddish-brown, but subsequently becomes colourless. No gas is given off, nor any peculiar odour perceptible. On evaporation at a gentle heat, it leaves a colourless radiately-crystalline mass, which is chlorhydroquinon; it is difficult to obtain it perfectly colourless.

Chlorhydroquinon forms stellate groups of prisms. It has a faint peculiar odour, a sweetish and at the same time hot taste; it melts very readily, and solidifies to a crystalline mass; heated still further, it is volatilized, and sublimes in colourless shining laminæ, but always with partial decomposition and carbonization, even in a cur-

rent of carbonic acid. It is very easily soluble in water, alcohol and æther, in the latter so readily that it deliquesces even in its vapour. Its aqueous solution, mixed with nitrate of silver, immediately reduces the silver to the metallic state, and at the same time the odour of quinon is perceptible. The solution becomes dark brownish-red with perchloride of iron, then milky, and deposits oily drops, which become converted in a short time into blackish-green prismatic crystals. It dissolves in caustic ammonia with a deep blue colour, which however soon passes into a greenish-yellow, and finally into a brownish-red.

The analyses of this body have led to the formula $C^{25}\,H^{10}\,O^{8}\,Cl^{2}$; it is therefore green hydroquinon + 2 equiv. chlorine.

It has already been mentioned that an analogous compound cannot be produced with iodine. Hydrocyanic acid is without action on quinon.

6. *Sulphohydroquinon.—Brown sulphohydroquinon* is formed when sulphuretted hydrogen is passed at the ordinary temperature into a saturated aqueous solution of quinon. The first bubbles colour the liquid of a beautiful red; a brownish turbidness then results, which soon increases to a considerable pure brown flocculent precipitate. It is immediately filtered, washed and dried; by the further action of the gas it would be converted into the following compound. Dry quinon is not altered by dry sulphuretted hydrogen gas.

It is a dark brown, pulverulent, amorphous substance, without taste or odour; it melts very readily and burns, giving off sulphurous acid. It dissolves very readily in alcohol with a dark yellowish-red colour; on evaporation it is left behind in a shining, transparent, amorphous state.

The analyses have led to the formula $C^{25}\,H^{11}\,O^{7}\,S^{4}$. If this composition be the correct one, it is formed by the addition of 4 equiv. of sulphuretted hydrogen to 1 equiv. quinon, and 1 equiv. hydrogen being eliminated with 1 equiv. oxygen as water. It is constituted as if it were a combination of 3 equiv. sulphuretted hydrogen with 1 of quinon, in which one-eighth of the oxygen is replaced by sulphur $= C^{25}\,H^{8}\,O^{7}\,S + 3HS$.

Yellow sulphohydroquinon originates when the preceding compound is suspended in water which is heated to about 135°, and sulphuretted hydrogen gas passed into it; it is then rapidly converted into an undefinable pale yellow powder, the whole liquid acquiring the appearance of milk of sulphur. A partial change begins already at the ordinary temperature, which renders it difficult to obtain the brown compound free from the yellow one. When the gas is passed into an almost boiling solution of quinon, a brown turbidness results in the first instance, which rapidly passes into yellowish-white, while at the same time a portion of the light-coloured sulphur compound is deposited in the form of a brownish, half-melted tenacious mass. This milky liquid passes turbid through the filter. With a high magnifying power the precipitated body is seen to consist of minute globules, which exhibit in an extraordinarily high degree the so-called molecular motion. But if a few drops of muriatic acid be

added to the liquid, it curdles as it were, and may now be filtered perfectly clear. The molecular motion has now entirely ceased, and it is seen that the minute particles have arranged themselves against each other in groups.

The sulphur compound, so prepared, forms when dry an undefinable yellow powder, which generally acquires a grayish-green tint by exposure to the air. It melts at about 212°, and solidifies to a brown amorphous mass. On ignition it diffuses the odour of sulphurous acid; it is soluble in alcohol, æther and acetic acid without residue, and with a reddish-yellow colour; on evaporation it is left in an amorphous state; it likewise dissolves in water, especially in boiling water; on cooling, the solution becomes turbid from the separation of the greater portion of the compound. On evaporating this solution, however, it soon undergoes decomposition, a greenish body containing sulphur separates, and finally colourless hydroquinon is obtained.

Dissolved in water, this body is well characterized by its property of being converted, when mixed with a solution of quinon, into the brown sulphohydroquinon, which separates in the form of a voluminous flocculent precipitate of a pure brown colour.

The yellow sulphohydroquinon is likewise formed when saturated colourless hydrosulphuret of ammonium is poured over quinon, which is thereby converted, with evolution of heat, into a yellow mass, which dissolves to a clear solution with a deep reddish-yellow colour in boiling water, which has been freed from air by long boiling. From this solution it is thrown down by muriatic acid as a yellowish-white flocculent precipitate. It is further produced when sulphuretted hydrogen is passed into green hydroquinon suspended in water.

The analyses have led to the formula $C^{25} H^{12} O^7 S^5$. It may therefore be regarded as a combination of 4 equiv. sulphuretted hydrogen with 1 of quinon, in which one-eighth oxygen is replaced by sulphur $= C^{25} H^8 O^7 S + 4HS$.

7. *Chlorosulphoquinon.*—There are two compounds of this kind, which contain sulphur and chlorine besides the elements of quinon. The brown chlorosulphoquinon is obtained as a flocculent precipitate when perchloride of iron is mixed with the solution of the yellow sulphohydroquinon, or the liquid which remains after precipitation by sulphuretted hydrogen, or when a certain amount of chlorine gas is passed into it. When dry it forms a light brown powder, melts readily, and dissolves in alcohol with a reddish-yellow colour; on evaporation it is left as an amorphous mass.

The orange-red chlorosulphoquinon has exactly the appearance of precipitated sulphuret of antimony. It originates from the preceding when chlorine gas is passed in excess into the liquid, when the brown colour of the precipitate is gradually converted into an orange-red, without its subsequently undergoing any other change by excess of chlorine. It is somewhat soluble in water, with a brownish-yellow colour; the solution reacts acid, but contains no sulphuric acid. It dissolves in alcohol, of a yellow colour. It melts

by heat, and is carbonized with disengagement of a powerful odour, which calls to mind that of certain volatile organic combinations containing chlorine. This body is, as the analyses appear to show, $C^{25}\,H^{6}\,O^{8}\,S^{4}\,Cl$.

It has been already mentioned that telluretted hydrogen gas does not produce similar combinations with quinon, but it converts it into colourless hydroquinon, with separation of tellurium. Arseniuretted and phosphuretted hydrogen gas are without any action on quinon. —*Götting. Gel. Anzeigen*, 1844, No. 117.

Borax in Bread.

One of the means employed to give bread made of bad meal a good appearance is borax. According to Duvillé, the bakers use about 4 oz. of borax to 100 lbs. of flour. To detect the borax in the bread, a considerable quantity should be extracted with water, the filtered extract clarified by boiling with albumen and strained; upon this concentrated sulphuric acid is added while stirring, and it is then placed aside. If borax is present crystals of boracic acid separate, which are now readily detected by their well-known reactions. —*Journ. de Chim. Méd.*, 1844, p. 145.

On some peculiar Reactions of the Bichloride of Mercury. *By* E. Millon.

The bichloride of mercury is not precipitated by the bichromate of potash, however concentrated the two saline solutions may be. But if a mixture of the two salts be made in the proportion of 1 equiv. of each, and dissolved in water with the assistance of heat, a very abundant crystallization takes place when the liquor cools, of a fine red, hard, and somewhat friable compound. This salt may be redissolved in water and recrystallized without decomposition.

The crystals are usually in radiate groups, and present singly the form of rectangular rhomboidal prisms with pyramidal summits. The powder of this salt is of a lively yellow; heat decomposes it, volatilizing some bichloride of mercury; the separation which thus takes place enables us to determine the composition of the salt; a very small quantity however of oxide of chrome is produced.

But the analysis is best performed by means of æther, which leaves intact the bichromate of potash. The form of the crystals is even preserved, although no trace of the bichloride remains. We thus find that the salt constantly loses 47·5 per cent. in weight, which leads to the following formula $2(CrO^{3})\,KO + HgCl$.

Absolute alcohol exercises an action analogous to that of æther.

It is not possible to produce a similar combination with the other metallic chlorides; the chloride of potassium furnishes a liquor of a blackish-brown colour, but it is impossible to separate any definite product.

This peculiar combination of the bichloride brings to mind the very singular manner in which the same compound behaves towards

acids; it is known, for instance, that concentrated or dilute sulphuric acid does not decompose the bichloride of mercury; the same is the case with nitric acid, in which some sublimate forms on the addition of hydrochloric acid. Nor does iodic acid precipitate the bichloride, notwithstanding that the iodate of the binoxide of mercury is perfectly insoluble. In short, the bichloride of mercury, notwithstanding its solubility, resists the action of strong acids, which always act on the elements of the dissolved chlorides, uniting with the base and setting free the hydrochloric acid.

But if the bichloride of mercury withstands the solicitations of affinity in the sense in which they ordinarily occur, it yields in a direction in which the affinity of the chlorides is rarely developed, forming a most remarkable contrast. Thus in the bichloride of mercury it is the chlorine which tends to separate from the metal, and the elements of water do not intervene in the reaction, even in an aqueous solution; the same tendency is therefore manifested when absolute alcohol is employed as solvent. I might here call to mind the organic decompositions in which the bichloride of mercury is reduced, but the peculiarity which I have indicated is not sufficiently distinct in them. The action of iodine on the bichloride of mercury exhibits clearly this special disposition of the combined chlorine and mercury. The iodine, in fact, displaces the chlorine, and forms at the same time chloride of iodine and iodide of mercury.

It might be supposed that this decomposition, the reverse of what takes place with respect to all the other metals, is owing to the insolubility of the bichloride of mercury; but such is not the case. The decomposition is effected precisely in proportion to the solubility of the bichloride of mercury in the medium employed as solvent; thus it is almost imperceptible when an aqueous solution of corrosive sublimate is employed, while with an alcoholic solution it is perfect. On evaporating alcohol containing some iodine and some of the bichloride in solution, beautiful red crystals of the biniodide are obtained, which led M. Lassaigne into error when he described* a very strange compound of bichloride of mercury and iodine which does not exist. He founded its existence on a very interesting reaction of the bichloride of mercury on the iodide of starch; this latter is decolorized by corrosive sublimate, which deprives it of the iodine to form biniodide of mercury and chloride of iodine, both without apparent action on the starch; but the blue colour may readily be made to reappear by a drop of iodide of potassium, which reacts on the chloride of iodine and sets the iodine at liberty.

This peculiar tendency led me to expect *à priori* that the iodide of mercury would not be attacked by chloride of iodine, and this is confirmed by experiment. In this respect the iodide of mercury forms an exception to all the other metallic iodides.

M. François Salvin, in a note on the solubility of iodine in saline liquids†, observed that the iodine disappeared in an aqueous solu-

* Ann. de Chim. et de Phys., 2e série, t. lxiii. p. 106.
† Institut, 2nd Janv. 1844.

tion of bichloride of mercury, but this remarkable and exceptional nature of the reaction did not engage his attention.

I must however add, that when solvents are not employed, the affinity of iodine for mercury does not exceed that of chlorine; thus in an atmosphere of chlorine, when this is in great excess, the biniodide of mercury is entirely converted into bichloride.—*Comptes Rendus*, Oct. 14, 1844.

PHARMACOLOGY.

Pharmaceutical Observations on the Ergot of Rye. By M. Pardu.

The best ergot is obtained from rye which is grown on dry, airy, elevated regions, and where the soil is sandy or chalky in character. When its form is somewhat elongated, and it is of a very dark, obscure colour, or if it has been gathered in plains or damp valleys, it should be regarded as of inferior quality. On chemical analysis, according to the experiments of Vauquelin, Wiggers and others, it yields nearly half its weight of oil, resin, wax, fatty matter and gum, all hydrogenous principles, and a little albumen and nitrogenous extract. If the season has been a wet one, or if the ergot has been gathered in moist places, these principles lose their relative proportions; and the spurred rye, approaching nearer in quality to good grain, contains but few oleo-resinous principles. It is worthy of remark, that this parasitic grain is only met with on the finest plants of rye in shady places, and towards the ends of fields recently cleared of wood, and where the carbonic principles and a rich soil abound.

Treatment by Æther.—On treating the ergot with æther, a fatty oil and fatty resinous matter are obtained. To separate these, it is sufficient to place them in a funnel; the fatty resinous matter rises and floats on the top. It is composed of cerine and white crystals of a bitter taste. The semi-resinous substance is of a reddish-brown colour, of the consistence of syrup, of an acrid, pungent and slightly bitter taste, has a nauseous narcotic odour, and is not saponifiable by either hydrate of potash or liquid ammonia. A pound of the ergot, with four times its quantity of æther at 75° of Beaumé, yields about an ounce. The oil is of a reddish colour, nauseous resinous odour and bland taste, but leaving behind a somewhat rancid impression. Its consistence is similar to that of castor oil. Treated with alcohol, its colouring resinous principle is dissolved, and a clear colourless oil, of a bland taste, is left. The æthereal resinous oil is not saponifiable, but that which is obtained either by heat or expression is so. Potash separates it into glycerine and two fatty matters, analogous to those of the common fixed oils.

Ammonia converts it into a soluble liniment, as it does the common oils. The same oil, deprived of resin, may be obtained by expression. In this way the author has obtained 4 oz. from 8 lbs. weight of the ergot, consequently the æther extracts a larger quan-

tity. On evaporating the alcohol in which the resinous matter has been dissolved, a semi-solid resin of an obscure coffee colour is obtained, of a nauseous, slightly acrid and bitter taste, *sui generis*, and a strong narcotic odour peculiar to the ergot of rye. A clearer oil, not resinous and almost inert, may be obtained by means of æther, if we employ ergot which has been previously boiled in concentrated alcohol, and thus deprived of its resinous principle.

Treatment by Alcohol.—If a pound of ergot be macerated for a day or more in 4 lbs. of alcohol at 38° or 40° of Beaumé, and afterwards gently boiled for a quarter of an hour by means of a water-bath, or, what is still better, allowed to remain for the space of an hour at the boiling-point, a tincture of a vinous colour is obtained, which on being evaporated at a temperature of 122°, or by the heat of the sun, yields nearly half an ounce of a semi-resinous substance, consisting of a true resin, segaline, a fatty oily matter, and an extract, vegetable osmazome, thus named before Berzelius had demonstrated its composition. On dissolving this alcoholic extract in water or æther, the nitrogenous principle remains in solution in the water and insoluble in the æther. If very concentrated alcohol be employed, and a large quantity of the extract be dissolved in the alcohol, then a resin is obtained separated from the fatty matter which remains. Finally, if we wish to procure the powder called *segaline*, the boiling alcoholic tincture must be prepared in the quantity of several pounds, and filtered at a high temperature. In this manner there will be obtained, on cooling, a mass of obscure, fat, gelatinous matter, which on being dissolved in æther loses part of its fatty matter, and leaves a sediment of a deep colour, which on being dried becomes reduced to a somewhat hard greasy powder, of a peculiar odour, and slightly bitter acrid taste. It is the *segaline* or *ergotine* which is obtained, he says, when the resinous extract is dissolved in a quantity of alcohol scarcely sufficient to saturate the resin; the segaline remains undissolved. The active principles are the oil, the resin, the segaline, the fatty resinous substance, and the spirituous and watery extracts.

Oil of Ergot.—It is essential in practice that a distinction be made between the oil obtained by expression and that deprived of resin. The latter is inert. The resinous oil is the most important, in fact the only one that should be employed in medicine. A few drops produce the most powerful effects. Similar effects may be obtained by means of the powder, but it must be given in larger doses.

Segaline or *ergotine* is a neutral powder, of a dull red colour, somewhat like cinchona, soft and unctuous to the touch, has a nauseous smell, similar to that of ergot in powder, and a pungent, acrid, bitter, nauseous taste. It is soluble in both concentrated acetic and sulphuric acids, and in pure hot alcohol; it is insoluble in water and æther. Its peculiar odour is increased by gentle heat; if strongly heated it becomes soft, and exhales an odour like that of roasted fish, and becomes carbonized. Different opinions have been entertained regarding its action. Wiggers regards it as the poisonous

principle of the ergot, whilst Bonjean believes it to be perfectly inert.

The author has made many experiments on this subject, which he details, from which it appears that the ergotine, prepared as directed, has an action similar to, but much less energetic than that of the resinous extract.

Infusion and Decoction.—The facts published by various authors, and those peculiar to M. Pardu himself, leave no doubt, he says, as to the true action of these preparations. He has satisfied himself, by comparative and incontestable experiments, that this action is much less energetic and certain than that of the simple ergot. The reason is, that by infusion or decoction the remedy is deprived of its most powerful elements, the resin and the oil.

M. Pardu draws the following conclusions from his experiments, pharmaceutical and clinical:—1st, that the active therapeutical, or poisonous agent of the ergot, is one and the same in all its preparations; 2nd, it is of a resinous nature; 3rd, it is to a modification of this principle that all the preparations of the medicine, including even the infusion, decoction and aqueous extract, owe their chief powers; 4th, the therapeutical or poisonous action of these preparations is in the ratio of the quantity of resinous principle they contain; 5th, the aqueous extract sometimes produces unfavourable effects, if given in large doses, corresponding to a given quantity of their resinous principle.—Abstracted from the *Lond. and Edinb. Med. Journ.* for August, 1844.

On Commercial Powdered Liquorice Root. By M. Ingenohl.

Of late there frequently occur in commerce powdered drugs, which are manufactured on a large scale in Holland and England; at first sight they seem from their external appearance to be very excellent. M. Wichmann recently called attention to a liquorice powder, which has become an object of commerce under the name of *Flores liquiritiæ*, which was adulterated with Dutch pink.

Some time ago I had an opportunity of convincing myself that the liquorice powder of commerce frequently contains a quantity of starch, and that on sifting it, small, tolerably hard granules remain behind, which swell in water and partially dissolve. Both the solution, as well as the swollen granules, are coloured indigo-blue by iodine water, which, together with their physical appearance, proves them to be sago.

Having read the above remark of M. Wichmann, I tested the same powder, which had been adulterated with starch, with muriatic acid for Dutch pink, and in fact it effervesced strongly, and the solution contained alumina and lime.

Such powdered drugs are frequently adulterated and impure, and should not be allowed to circulate in commerce.—*Arch. der Pharm.*, xxx.

CHEMICAL PREPARATIONS.

On a simple Method of preparing the Iodide of Ammonium, with some Account of its Properties. *By* Dr. C. Herzog.

For some time past the iodide of ammonium has been occasionally prescribed, which has induced me to try and find out a simple and convenient mode of preparing it.

This compound cannot be obtained by bringing iodine and solution of ammonia together, since iodide of nitrogen is cotemporaneously produced, a highly dangerous body on account of its explosive nature.

It may be prepared,—1st, by neutralizing caustic ammonia with hydriodic acid; 2nd, by decomposing the protiodide of iron with carbonate of ammonia; and 3rd, and best, by conveying iodine into sulphuret of ammonium.

With respect to the first method, it requires the preparation of hydriodic acid, by passing sulphuretted hydrogen into solution of iodine, neutralizing the liquid and evaporating. In the latter operation some iodide of ammonium is very easily decomposed, ammonia being given off, while the liberated iodine colours the liquid, which acquires an acid reaction. In order to remove the reddish-brown colour and the acidity, the hydrosulphuret of ammonium must be employed, since iodide of nitrogen is easily produced on the addition of pure ammonia.

The second method, which has moreover the inconvenience that the liquid cannot be heated strongly on or after precipitation*, as in the preparation of iodide of potassium, so as to ensure a better separation of the protocarbonate of iron, easily leads to loss, and moreover requires on evaporation of the salt treatment with hydrosulphuret of ammonium.

It is evident, from the preceding methods of preparation, that the presence of hydrosulphuret of ammonium is requisite, although only in small quantities. It may easily be prepared on a large scale by passing sulphuretted hydrogen into solution of ammonia; it is, however, necessary to observe that the ammonia be completely saturated, and no longer precipitate a solution of a salt of magnesia.

Iodine is conveyed in small portions† into this liquid, constantly stirring until the sulphur, which at last is precipitated in flakes, has a gray appearance, and the liquid begins to become somewhat turbid; it is then filtered‡, the sulphur well-washed, and the liquid evaporated, first over the spirit-lamp, and then to dryness on a steam-bath. The dry powder must be immediately preserved in black well-closed bottles. The liquid easily becomes coloured and acid on evapora-

* The liquid becomes acid on the application of heat, and then readily takes up more iron.

† Larger quantities would cause the liquid to become strongly heated.

‡ In case the liquid does not pass through clear, it is only requisite to mix some charcoal with it and then to filter.

tion if an excess of hydrosulphuret of ammonium is not present; if this happen, a few drops should be added, when it frequently happens that it must be filtered again. It may also be obtained in crystals on evaporating till a film forms on the surface; this however is always accompanied with great loss, as a small portion of mother-ley contains much salt, and on drying the crystals by exposure to the air, they partially deliquesce and become coloured.

For 228 grs. of iodine I required 405 of hydrosulphuret of ammonium and obtained 258 grs. of dry iodide of ammonium, which agrees with the theoretical amount to within 3 grs.

The salt crystallizes from concentrated solutions in small cubes, has a highly irritating saline taste, becomes readily moist and yellow on exposure to the air, and deliquesces in a short time. It dissolves in equal parts of water at 68° F., and in 4½ parts of absolute alcohol at the same temperature. The aqueous solution of the iodide of ammonium likewise becomes coloured on exposure to the air, although much slower, parts with ammonia, possesses nearly always an acid reaction, and it is very difficult, even on adding ammonia constantly during evaporation, to obtain a perfectly neutral salt. It volatilizes on the application of heat without melting and decrepitating, but with more difficulty than sal-ammoniac, and undergoes a partial decomposition. It behaves towards reagents like the other compounds of iodine, only that it presents some anomalies from its being an ammonia salt.

Composition.—228 grs. of iodine precipitated, on the decomposition of the hydrosulphuret of ammonium, 28·89 grs. of sulphur, which contained only traces of iodine, consequently 1 equiv. of sulphur had been separated for each equiv. of iodine, for—

1578·29 (= 1 equiv.) iodine : 201·165 (1 equiv.) S = 228 : x
= 29·05 sulphur.

The iodide of ammonium is therefore represented by the formula $I^2 + N^2 H^8$, or $I^2 H^2 + N^2 H^6$, and the atomic number = 1805·24. —*Archiv der Pharm.* for October 1844.

Adulterated Nitric Acid.

According to M. Ricker, nitric acid occurs in commerce, to which some sulphuric acid has been purposely added in order to increase the specific gravity. He found in a sample 7 per cent. of the hydrate of sulphuric acid.—*Jahrb. für Prakt. Pharm.*, ix. p. 21.

Preparation of the Oxide of Antimony. By C. Frederking.

The preparation of oxide of antimony from metallic antimony with nitric acid does not always prove successful. With the same proportions of materials, and with the same temperature, I have sometimes obtained oxide of antimony with antimonious acid, sometimes pure oxide. I have found by observation that antimonious acid is constantly formed when the nitric acid contains more or less

nitrous acid; this view, however, requires further confirmation. Dissolving sulphuret of antimony in muriatic acid, for the purpose of preparing algaroth powder, is by far too slow a process. Brandes' method is more ready and expeditious.

On oxidizing some metallic antimony with concentrated sulphuric acid in a porcelain basin, I was compelled to digest it for several days before the mass became whitish, and nevertheless the whole of the antimony had not become oxidized. The oxidation of the metal resulted in a far less time on allowing 15 oz. of finely-pulverized *Regulus antimonii* with 36 oz. of concentrated sulphuric acid to stand for 12 hours in an *iron* caldron, and then applying a slowly-increasing heat, frequently stirring. If this latter operation is performed under a good draught chimney, the evolution of the sulphurous acid gas is supportable. Heat should be applied until the mass forms a grayish-white powder; it is then conveyed into a pan, having been previously finely powdered, 30 lbs. of hot water poured over it, and frequently agitated. The oxide is allowed to settle, the liquid poured off, the residue washed first with water, then with a solution of carbonate of soda, and lastly with pure water. After drying, the oxide weighs about 16 oz., is grayish-white, and dissolves almost entirely in cream of tartar. It was found to be free from iron, but the acid liquid contained some iron in solution. It is probable that the antimony on its oxidation forms an electric circuit with the metallic iron, which thus proceeds more rapidly.—*Archiv der Pharm.* for October 1844.

PATENT.

Patent granted to Antoine François Jean Claudet, London, *for Improvements in the Process and Means of obtaining the Representation of Objects of Nature and Art.*

These improvements consist in rendering the Daguerreotype picture susceptible of producing, by printing, a great number of proofs or copies; thereby transforming it into a complete engraved plate.

The process is established upon the following facts, which have come to the knowledge of the inventor:—

1. A mixed acid, composed of water, nitric acid, nitrate of potash and common salt, in certain proportions, being poured upon a Daguerreotype picture, attacks the pure silver, forming a chloride of that metal, and does not affect the white parts, which are produced by the mercury; but this action does not continue long. Then, by a treatment with ammonia (ammonia containing already chloride of silver in solution is preferable for this operation), the chloride of silver is dissolved and washed off, and the metal being again in its naked state, or cleansed from the chloride, it can be attacked afresh by the same acid. This acid acts better warm than cold.

2. As all metallic surfaces are soon covered (when exposed to the

atmosphere) with greasy or resinous matters, it is necessary, in order that the action of the acid upon the pure silver should have its full effect, for the surface to be perfectly purified; this is effected by the employment of alcohol and caustic potash.

3. When a Daguerreotype picture is submitted to the effect of a boiling concentrated solution of caustic potash, before being attacked by the acid, the state of its surface is so modified, that the acid spares or leaves, in the parts which it attacks, a great number of points, which form the grain of the engraving.

4. When the effect of the acid is not sufficient, or, in other words, if it has not bitten deep enough, the effect is increased by the following process:—Ink the plate as copperplate printers do, but with a siccative ink; when the ink is sufficiently dry, polish the white parts of the plate, and gild it by the electrotype process; then wash it with warm caustic potash, and bite in with an acid, which will not attack the gold, but only the metal, in those parts which, having been protected by the ink, have not received the coating of gold. By these means the engraving is completed, as by the action of the acid alone it is not generally bitten in deep enough.

5. To protect the plate from the effects of wear, produced by the operation of printing, the following process is employed:—The surface of the plate is covered with a very thin coating of copper, by means of the electrotype process, before submitting it to the operation of printing; and when that pellicle or coating of copper begins to show signs of wear, it must be removed altogether, by plunging the plate in ammonia or in a weak acid, which, by electro-chemical action, will dissolve the copper without affecting the metal under it; the plate is then coppered again by the same means, and is then ready for producing a further number of impressions. This re-coating operation may be repeated as many times as may be required. The following is the description of the whole process, which is divided into two parts, consisting of a preparatory and finishing process:—

Preparatory Engraving.—For this operation, which is the most delicate, it is necessary to have,—1st, a saturated solution of caustic potash; 2nd, pure nitric acid at 36° of the areometer of Beaumé (spec. grav. 1·333); 3rd, a solution of nitrite of potash, composed of 100 parts of water and 5 parts of nitrite by weight; 4th, a solution of common salt, composed of water 100 parts and salt 10 parts by weight; 5th, a weak solution of ammoniacal chloride of silver, with an excess of ammonia; the ammoniacal chloride of silver must be diluted with 15 or 20 parts of pure water; in the description of the process this solution will be called ammoniacal chloride of silver; 6th, a weak solution of ammonia, containing four or five thousandths of liquid ammonia; this solution will be called ammoniacal water; 7th, a weak solution of caustic potash, containing four or five thousandths of the saturated solution, which will be called alkaline water; 8th, a solution composed of water 4 parts, saturated solution of potash 2 parts, alcohol 1 part, all in volume; this solution will be called alcoholized potash; 9th, acidulated water, composed of water 100 parts and nitric acid 2 parts, in volume. Be-

sides, it is necessary to have three capsules or dishes, made of porcelain, large enough to contain the plate, and covered with an air-tight piece of ground plate-glass, and two or three more capsules, which do not require to be covered; two or three glass funnels, to wash the plate; and two or three glass holders, in the shape of a spoon or shovel, by which the plate is supported when put in and taken out of the solution, without touching it with the fingers.

The Daguerreotype plate is submitted to the engraving process, after having been washed in the hyposulphite of soda, and afterwards in distilled water.

First Process for biting in or engraving the Plate.—The following solutions must be put in the capsules, in sufficient quantity, so as to entirely cover the plate:—1st, acidulated water; 2nd, alkaline water; 3rd, alcoholized potash, in covered capsules; 4th, caustic potash, in covered capsules; 5th, distilled water.

The plate being put upon the glass-holder or spoon, is plunged in the acidulated water, and agitated during a few seconds, then put into a glass funnel, and washed with distilled water. It is taken again with the glass spoon, and plunged in the capsule containing alcoholized potash. This capsule is covered with its glass cover, and then heated, by means of a spirit-lamp, to about 144° Fahr. The plate must remain in the capsule half an hour, during which the solution is heated now and then, and agitated. During that time the following acid solution, which will be called *normal acid*, must be prepared; it is composed as follows:—Water 600 parts, nitric acid 45 parts, solution of nitrite of potash 12 parts, solution of common salt 45 parts. These proportions are in volume. The normal acid must be poured in a capsule, covered with its glass cover, and a sufficient quantity must be kept in the bottle.

When the plate has been immersed in the alcoholized potash during half an hour, it is taken out of the solution by means of the glass holder, and immediately plunged in the alkaline water, and agitated pretty strongly; from thence it is put in distilled water. (A)

This being done, the plate is plunged in the acidulated water, and moved about therein for a few seconds; it is then put into the normal acid. When the plate has been immersed a few seconds in the acid, it is taken out by means of the glass holder, taking care to keep it as much as possible covered with the solution, and it is immediately placed horizontally upon a stand, and as much acid as the plate can hold is poured upon it from the bottle; it is then heated with a spirit-lamp, but without attaining the boiling-point. During this operation it is better to stir or move about the acid on the plate by pumping it, and ejecting it again, by means of a pipette or glass syringe; after two or three minutes the acid is thrown away, the plate is put in the glass funnel, and there well washed with water, and afterwards with distilled water. (B)

Then, without letting the plate dry, it is put upon the fingers of the left-hand, and with the right-hand some ammoniacal chloride of silver, which is moved about the surface by balancing the hand, is poured upon it; the solution is renewed until the chloride, formed

by the action of the acid, is dissolved; the plate is then washed by pouring upon it a large quantity of ammoniacal water, and afterwards some distilled water. (C)

Without allowing the plate to dry, it is then put in the caustic potash, and the capsule being placed upon the stand, the potash is heated up to the boiling-point; it is then left to cool (D); and beginning again the operations described from A to D, a second biting is obtained; and by repeating again the operations described in A and B, a third biting is produced. The plate is then dried; in this state the black parts of the plate are filled with chloride of silver.

The plate is then polished until the white parts are perfectly pure and bright. This polishing is done with cotton and "ponce" (pumice stone); afterwards, the chloride of silver, filling the black parts, is cleansed by the means described in B and C. The plate is dried, but before drying it is well to rub the plate slightly with the finger, in order to take off from the black parts any remains of an insoluble body which generally adhere to it. The preparatory engraving is then finished, and the plate has the appearance of a very delicate aquatint engraved plate, not very deeply bitten in.

Nevertheless, if the operation has been well managed, and has been successful, it is deep enough to allow the printing of a considerable number of copies.

Note.—Sometimes, instead of treating the plate with the boiling potash in the capsule, a similar result may be obtained by placing the plate upon the stand, covering it with the solution, and heating it by means of a spirit-lamp, until by evaporation the potash becomes in a state of ignited fusion. By this means the grain is finer, but the white parts are more liable to be attacked.

Last Operation of biting in.—This operation requires some of the reagents before-named, and also—

1. A siccative ink, made of linseed oil, rendered very siccative by boiling it sufficiently with litharge; it may be thickened with calcined lamp-black.

2. An electrotype apparatus, and some solutions fit to gild and copper the plate.

Means of operating.—The plate must be inked as copperplate printers do, taking care to clean off the white parts more perfectly than usual; the plate is then to be placed in a room sufficiently warm until the ink is well dried, which requires more or less time according to the nature of the oil employed. The drying of the oil may be hastened by heating the plate upon the stand with the lamp, but the slow process is more perfect and certain.

When the ink is well dried, the white parts are cleaned again, by polishing the plate with cotton and ponce, or any other polishing powder; a ball of cotton, or any other matter, covered with a thin piece of caoutchouc or skin, can be used for this purpose. When polished, the plate is ready to receive the electro-chemical coating of gold, which will protect the white parts.

Gilding.—The gilding is obtained by any of the various processes

of electrotyping which are known. The only indispensable condition is, that the surface obtained by the precipitation must not be liable to be attacked by any weak acid; a solution answering this purpose is made of 10 parts (by weight) of ferrocyanide of potassium, 1 part of chloride of gold, and 1000 parts of water, used with a galvanic battery. During the gilding the plate must be turned in several positions, in order to regulate the metallic deposit. In some cases the gilding may be made more perfect, if the plate is covered with a thin coating of mercury before being put in the gilding solution.

When the plate is gilded, it must be treated with the boiling caustic potash, by the process already indicated for the preparatory engraving, in order to cleanse it from all the dried oil or ink which fills the hollows. The plate is then washed and dried, and when the oil employed has been thickened with the lamp-black, the surface of the plate is rubbed with crumb of bread, in order to cleanse and take off the black remaining; then, the white parts being covered and protected by a varnish not liable to be attacked, and the black parts being uncovered and clean, the plate can be bitten-in by aquafortis, according to the ordinary process used by engravers.

This operation must be done upon the stand, and not by immersing the plate in the solution.

Before this last biting-in, if the preparatory engraving has not succeeded well, and the plate still wants a sufficient grain, it can be given by the various processes of aquatint engraving.

Before submitting the plate to the operation of printing, in order to ensure an unlimited number of copies, it is necessary, as before stated, to protect it by a slight coating of copper, which is obtained by the electrotype process; otherwise the printing would soon wear the plate. This coating must be kept very thin, lest the fineness of the engraving and the polish of the white parts should be destroyed. In this state the plate can be delivered to the printer.

After a certain number of impressions have been obtained, it will be perceived that the coating of copper is worn in some places; then this coating must be removed, and a fresh one applied in its place. For this purpose, the plate must be purified and cleansed by warm potash, and plunged in a weak acid composed as follows:—Water 600 parts, nitric acid 50 parts, nitrous acid of engravers 5 parts, all in volume. This acid will dissolve the coating of copper, and the plate being coppered again, by the same means as before, may be again submitted to the operation of printing; and as nothing can prevent the success of a repetition of the same operation, any number of impressions may be obtained. The coating of copper can also be removed by caustic ammonia.

The Daguerreotype plate engraved by this process may be also reproduced and multiplied by the electrotype process, the same as any other engraved plate.—Sealed Nov. 21, 1843.

THE CHEMICAL GAZETTE.

No. LI.—December 2, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Examination of the Berries of Coffee. By M. Rochleder

The berries of coffee contain the following substances:—

1. *Vegetable Fibre.*—This hard, horny substance is obtained pure by reducing the berries, after they have been dried for several weeks at a temperature of 212°, to powder by repeated pounding, separating the fifth part by suspension in æther, boiling this successively with æther, alcohol, water, dilute caustic potash, dilute muriatic acid, and lastly, exhausting it again with water, forming the swelled residue into a paste with water, adding to this absolute alcohol, boiling, filtering and drying. In this manner a white powder is obtained void of smell and taste, which is insoluble in æther, alcohol, water, dilute acids and alkalies. On roasting it, it merely smells like wood, affords acetic acid, &c., and, finally a coal of difficult combustion. No sugar is produced even by long-continued boiling with moderately-concentrated sulphuric acid, but only a dark solution, in which water produces a precipitate. The fibre contained 0·67 per cent. ash, and 47·48 C, 6·53 H. It has not therefore the composition of true woody fibre, but that of the woody incrustation described by Payen*.

2. *Fat.*—Ordinary æther affords with the berries of coffee a golden-yellow tincture, which contains other substances besides fat. The æthereal extract is shaken with a fifth part of its volume of water, this removed by means of a siphon or a pipette, and the operation repeated until the water no longer deprives the æther of anything further. The aqueous solution gives with salts of lead a yellow precipitate, which consists of several acids, contained in the berries, in combination with oxide of lead. After the aqueous solution has been freed from these acids, it contains solely caffeine.

The æthereal extract of the berries, after shaking with water, contains only fat, accompanied by an extremely small quantity of a substance containing sulphur, which cannot be separated from the fat.

After removal of the æther by distillation, a yellow-coloured buttery mass is obtained, which is a mixture of a solid with a small quantity of a fluid fat. The former is crystalline, and is obtained,

* See Chem. Gaz., p. 510.

although not in a pure state, directly from the pulverized berries, on boiling them with an equal volume of spirit and concentrating the filtered solution to within one-eighth by distilling off the alcohol. On cooling, the liquid becomes turbid, and deposits the solid fat in flakes, which melt on the application of heat, and solidify to a brown friable mass.

To prepare the fat acids contained in the fat of the coffee berries, the above-mentioned buttery mass, remaining after removal of the æther, and which must have been purified from all substances soluble in water, is boiled with potash to a clear gelatine, the soap separated by means of salt, and the soda soap dissolved in water and decomposed with dilute sulphuric acid. The fat acids separate on the surface as a yellow oil, which is freed by water from adherent impurities. On cooling, this oil solidifies to a faintly yellow-coloured mass, which melts between 115° and 117° Fahr.

To combine the two fat acids with oxide of lead, they were saponified with carbonate of soda, the soap dissolved in alcohol, filtered from the excess of carbonate, and the alcoholic solution mixed with a large quantity of water. After expelling the greater portion of alcohol by boiling, it was precipitated with sugar of lead, and the plaster-like precipitate washed with water.

The author endeavoured to separate the oleate of lead from the combination of the solid acid, by treating this precipitate with æther; it was however found to be impossible from the lead salt swelling into a jelly, which could not be filtered.

The separation of the mixture was effected by boiling it with alcohol, which dissolved both the lead salts, but on cooling only retained the oleate of lead in solution, while the second salt was deposited as a white powder. On distilling off a portion of the alcohol, the mother-ley deposited still more of this salt, which was collected on a filter and washed with cold weak spirit. By decomposing with sulphuretted hydrogen the oleate of lead dissolved in the alcohol, and distilling off the alcohol in the water-bath, the oleic acid is obtained, but not entirely free from solid acid.

The more insoluble lead salt was suspended in a mixture of alcohol and æther, and decomposed by a current of sulphuretted hydrogen. The liquid filtered from the sulphuret of lead afforded, on driving off the alcohol and æther in the water-bath, a white, brittle, crystalline mass, which could not be distinguished in its properties from the hydrate of margaric acid. To remove every trace of adherent oleic acid, it was recrystallized from alcohol, that which first separated recrystallized, and this operation repeated five times. After expelling the alcohol in the water-bath, the melting-point of the mass was constant at 137° Fahr. The acid consists of 75·4 per cent. C, 12·3 H, 12·3 O. The silver salt, dried at 212°, contains 31·37 oxide of silver. The acid is therefore *palmitic acid.*

3. *Caffeine* is best obtained by shaking the æthereal extract of the berries with water, precipitating the aqueous solution with basic acetate of lead, removing the excess of lead, and crystallizing the filtered solution. The caffeine is *entirely* extracted by æther.

4. *Legumine.*—As is well known, Peligot discovered in tea a proteine compound resembling caseine*. The demonstration of legumine in coffee again confirms the remarkable analogy between tea and coffee. The legumine from the berries of coffee is obtained by macerating their powder from 3 to 4 hours in water, then filtering the brownish liquid and precipitating with acetic acid. The precipitate is washed by decantation with weak spirit, exhausted with boiling alcohol and æther, and dried. It then forms a faintly yellowish substance, which may be reduced to powder, puffs up on being heated, smelling of burnt horn, but leaving scarcely a trace of ash behind. The analysis gave 52·64 C, 6·97 H. By the above treatment, however, only the smallest portion of the legumine of the berries is obtained; the lime present seems to hinder the solubility of the legumine in the water. Carbonate of potash affords a saturated yellow, subsequently green solution, from which acetic acid precipitates the legumine in *blue* flakes, which again become green by the addition of an alkali. These colours depend on the presence of some acid.

It is owing to the legumine that silver vessels, in which the berries of coffee are boiled with alkalies, become black. The hot infusion of roasted coffee contains *no* legumine. It is moreover owing to the legumine that coffee berries, to which hot water has been added, pass after a time into fermentation, affording an acid liquid, which, saturated with chalk, filtered, freed from the excess of chalk and distilled with a little sulphuric acid, affords a product which smells faintly of alcohol and roses, which odour is not dispelled by acids and alkalies.

5. The substances which are precipitated by sugar of lead and basic acetate of lead from the aqueous solution of the æthereal extract, as well as from the aqueous decoction, after removal of the legumine by acetic acid, the author intends to make the subject of a second treatise.—Liebig's *Annalen*, l. p. 224.

On two new Series of Salts. *By* M. E. Fremy.

In a former communication† I described two new acids, which are formed in the reaction of sulphurous and nitrous acids on bases; I showed that these acids, which are of inorganic origin, present a certain analogy with the nitrogenous organic bodies, and when heated disengage ammoniacal vapours.

I have endeavoured to extend these researches, which appear to me to be of considerable interest; and I am now able to state, that the elements of sulphurous acid, of nitrous acid and of water, unite in presence of an alkaline base in different proportions, producing four distinct kinds of salts, which contain acids formed of oxygen, sulphur, hydrogen and nitrogen.

It is no longer an isolated instance, but a series of reactions, which appears to constitute an entirely new class of phænomena.

* Chem. Gaz., vol. i. p. 561. † Ibid, present volume, p. 459.

By examining in a general manner the action which two acids exercise on the same base, I discovered that if, in a great number of circumstances, acids share the base with each other to form different salts, it may often happen that the two acids unite in presence of the base to constitute a single molecule of acid. This case especially occurs when the two acids decompose each other in the isolated state.

To demonstrate this important property, I took as example the two acids, sulphurous and nitrous, which, as is known, are transformed under the influence of water into sulphuric acid and into deutoxide of nitrogen.

If a current of sulphurous acid is passed into a solution of nitrite of potash which contains an excess of alkali, the liquor immediately becomes as it were gelatinous, and deposits a white salt, which resembles the neutral stearate of potash. This compound presents none of the characters of the salts formed by the acids of nitrogen or of sulphur. When heated it disengages red vapours, sulphurous acid and ammonia. It contains a new acid, formed of oxygen, sulphur, hydrogen and nitrogen, which I have called *sulphonitrous acid.*

This acid can only exist in combination with bases; when a sulphonitrite is treated with an acid, it disengages immediately deutoxide of nitrogen and gives rise to a sulphate.

Sulphonitrous acid combines with all the bases; I will only mention at present the sulphonitrite of potash, which will serve to characterize the other sulphonitrites.

Sulphonitrite of Potash.—This salt is very soluble in water, insoluble in alcohol, and has a strong alkaline reaction. It is suddenly decomposed by heat, with production of sulphurous acid, ammonia, red vapours, and leaves a residue of neutral sulphate of potash; under the influence of acids it disengages deutoxide of nitrogen; it is rapidly oxidized by chlorine or nitric acid. The salt may be represented by the formula $2SO^3$, $2SO^2$, NO^3, $H^2O^2 + 3KO$.

Supporting my views by the valuable observations which M. Chevreul has made respecting the *rational formulæ* of compound bodies, I will here only observe that the sulphonitrous acid is formed of four elements, which represent sulphuric acid, sulphurous acid, nitrous acid and water.

I now pass to the second class of compounds, which originates in the reaction of sulphurous acid on nitrites.

When the sulphonitrite of potash is treated with a fresh quantity of sulphurous acid in presence of an excess of potash, it is completely transformed into another salt, which contains a new acid, which I have named *sulphonitric.* This acid, which is similar to the preceding one, can only exist in combination with the bases; but it forms some salts which differ entirely from the sulphonitrites. The sulphonitrate of potash characterizes this new class of compounds extremely well. This salt is indeed remarkable from its beautiful crystallization; it is soluble in water, and often crystallizes in broad rhomboidal tables; its reaction is alkaline and its taste slightly

caustic; neither sulphuric nor hydrochloric acid decomposes it; this property distinguishes it from the sulphonitrite, which is, as I have before said, destroyed by acids. It has the following composition:—$2SO^3$, $3SO^2$, NO^3, H^2O^2, 3KO.

By comparing this formula with that of the sulphonitrite, it is seen that the two acids in these salts only differ by 1 equiv. of sulphurous acid; it is readily conceived, therefore, how the sulphonitrite is transformed into sulphonitrate under the influence of sulphurous acid.

Sulphonitric acid forms crystallizable salts with some of the other bases, and even some double salts.

To obtain the third series of salts, the sulphonitrate of potash, containing an excess of base, must be treated with sulphurous acid. The liquor, which was at first perfectly clear, soon deposits long silky needles of sulphammonate of potash. It will be recollected that this salt, which was described on a previous occasion, is characterized by its insolubility in an alkaline liquid, and its rapid conversion into sulphate of ammonia and bisulphate of potash when boiled in water.

This salt may be represented by two *equivalent compositions*; the formula $7SO^3$, NH^3, SO^2, 4KO exhibits its decomposition into acid sulphate of potash and sulphate of ammonia; the formula $2SO^3$, $6SO^2$, NO^3, H^2O^2, 4KO establishes a relation between the sulphammonate of potash and the preceding salts, and moreover shows that it only differs from the sulphonitrate of potash by some sulphurous acid and potash.

In short, when the sulphammonate of potash is treated with water at 104°, it is deprived of 1 equiv. of bisulphate of potash while forming the new salts which I have called *sulphamidates*, and which differ in all their properties from the preceding.

The preceding facts prove therefore that sulphurous and nitrous acid, which are so easily decomposed in water, unite in the presence of water and of potash, to form four different kinds of salts.

These bodies are not only interesting from their production, but also from their aggregate properties and the mobility of their elements, which bring them near to organic substances; I have ascertained that these new salts may be modified by chemical agents without being entirely decomposed.

I think that I may here state positively, that other acids may, like the nitrous and sulphurous acids, unite in presence of a base to constitute a molecule of a new acid; and that consequently this class of phænomena must enrich science with a great number of new compounds.—*Comptes Rendus* for Oct. 21, 1844.

On Cellulose, according to the Researches of MM. Payen and Fromberg.

Payen found, on repeating the analyses of oak and birch wood, that the oxygen and hydrogen were not contained in it exactly in

the same proportion as in water. He further supposes that a peculiar substance, which he terms *matière incrustante*, is contained in the tissues of plants, the presence of which explains the decrease in the amount of carbon when the vegetable tissues are treated with solvents, especially with alkalies. The above kinds of wood, freed by means of strong nitric acid from all soluble substances, afforded him the following results:—

	Before treatment.		After treatment with nitric acid.
Carbon	54·44	51·35	43·85
Hydrogen	6·24	6·25	5·86
Oxygen	39·32	39·50	50·28

The proper tissue of plants, the cellulose, is not acted upon, according to Payen, by nitric acid of 1·5 spec. grav., which is likewise Dutrochet's opinion. Pelouze, however, states that it is converted into xyloidine. Payen now supposes that the substance deposited in layers in the ligneous cells is distinct from the peculiar substance of the cells, and considers this to be the reason of the different results which have been obtained in the analysis of lignine from different kinds of wood. The so-called incrusting substance is represented, according to Payen, by the formula $C^{35} H^{24} O^{20}$; it differs from cellulose by its producing red vapours with nitric acid, and being deeply coloured by sulphuric and muriatic acids. Pure cellulose, dissolved in strong sulphuric acid, behaves like dextrine towards polarized light. Little or none of the incrusting substance is said to be contained in the medullary cells.

In a subsequent paper Payen communicates the analytical results he obtained with several different plants, and parts of plants, after they had been exhausted with weak caustic soda. He analysed, for instance, the ovules of the almond, pear and apple tree, and of *Helianthus annuus*, the membranous substance of the cambium, and the cellular tissue of the cucumber, the pith of the elder and of the *Æschynomene paludosa*, cotton, the medullary tissue of the oak, the inner tissue of the leaves of *Agave americana*, the skeleton of a wasp's nest, coniferous wood, Iceland moss, several *Confervæ*, and also inuline.

The final result of Payen's researches may be summed up as follows:—

Cellulose, starch, dextrine and the two inulines are isomeric; medulline, fungine and lichenine are not peculiar substances, but identical with cellulose; gluten does not form a tissue, but is a peculiar compound contained in the cells of the seed-envelopes of the Cerealia.

To test some of these statements of Payen, Fromberg made the following experiments:—Iceland moss was extracted with weak caustic solution of soda, and then exhausted with boiling water until the decoction was no longer coloured blue by tincture of iodine, and finally treated with alcohol of 0·879, æther and dilute muriatic acid. The residue, washed well with water, was submitted to analysis (I.). For analysis (II.), the substance was again treated with

caustic soda, dilute muriatic acid, æther and alcohol. They afforded—

	I.	II.
Carbon	46·68	45·85
Hydrogen	6·18	6·22
Oxygen	47·17	47·93

Agaricus albus, well-dried, was exhausted with boiling water until iodine no longer presented any reaction; it was then treated with a warm solution of caustic soda until muriatic acid produced no precipitate in the solution. After washing with water, the mass was treated as before with alcohol of 0·879 spec. grav., æther and dilute muriatic acid. Two analyses gave—

	I.	II.
Carbon	45·47	45·28
Hydrogen	6·29	6·27
Oxygen	48·14	48·45

The following numbers were obtained after repeating the above treatment:—

	I.	II.	III.
Carbon	43·77	44·09	43·95
Hydrogen	5·90	6·25	6·21
Oxygen	50·23	49·66	49·84

Beet, cabbage, &c., afforded, on similar treatment, quite the same results, which in general agree with those obtained by Payen. Fromberg however does not admit all the conclusions of Payen, it having been decidedly proved, relatively to the composition of these bodies, that inuline contains half an atom more water than amylum.

We here insert some analyses by Dr. A. W. Hoffmann, made in the Giessen laboratory with linen which had been boiled in strong muriatic acid until it fell to a fine powder. After washing with water and drying, the analyses afforded—

	I.	II.	Cellulose.
Carbon	44·56	43·86	44·56
Hydrogen	6·62	6·50	6·18
Oxygen	48·81	49·64	49·38
	100·00	100·00	100·00

Ann. der Chem. und Pharm., xlviii. p. 353.

Phosphuret of Copper.

If, according to M. Casoria, water and phosphorus are boiled in a flask, and the vapours conducted into a solution of a salt of copper, a black precipitate separates, the composition of which is represented by Cu^2P; it can be fused, with the exclusion of the air, to a reddish-yellow sphere of metallic lustre. The same compound is formed in small quantity when solutions of copper salts are boiled in alcohol or æther with phosphorus; sulphate of copper alone forms an exception; in neither case does it afford phosphuret of copper, but only pure copper.—Berzelius, *Jahresbericht*, xxiv. p. 144.

On the Nature of Fulminic Acid. By M. Berzelius.

As is well known, this acid has been regarded, in accordance with the no less dangerous than meritorious analysis of the fulminate of the protoxide of mercury executed conjointly by Gay-Lussac and Liebig in 1823, as an isomeric modification of cyanic acid, whose salts have absolutely the same composition as the corresponding cyanates. However, two circumstances in the fulminates have shown that they differ essentially from the cyanates; first, by the powerful explosion with which they are decomposed on the slightest application of heat; and secondly, that of the metallic oxide, regarded as the base in the salt, only half can be separated by alkalies; and that when the salt contains oxide of silver or protoxide of mercury, only half of the amount of metal is precipitated by chloride of potassium or chloride of sodium. We have, it is true, some examples of salts with so decided a tendency to form double salts, that this tendency withstands the affinity of stronger bases or acids, for instance hyposulphites with alkaline base, even in excess, dissolve chloride of silver and iodide of silver, so that this last circumstance proves of itself nothing; but when the silver salt is exactly decomposed with chloride of potassium, and the chloride of silver removed, a salt separates from the evaporated solution, which, according to the received view of the nature of these salts, is AgO, CyO + KaO,CyO, which does not explode less easily or with less force than the simple silver salt. From this it appears that the fulminating property must depend upon something else than a sudden combustion at the expense of the oxygen of the metallic oxide; for were this the case the potash salt would have lost a considerable portion of the fulminating force, since none of the acid can be burnt at the expense of the potash. That which fulminates in the potash salt can consequently not be AgO, CyO. After having quite recently become acquainted with combinations of the metals with nitrogen, which like chloride of nitrogen and iodide of nitrogen are decomposed at an elevated temperature, or by a blow, or by friction, instantaneously into their constituents, with light and with a most powerful detonation, we might be induced to suspect that the above salts may contain a metallic nitruret which is the cause of these phænomena. This suspicion gains strength from Mitscherlich's well-known discovery, that nitruret of mercury can combine with perchloride of mercury and with perbromide of mercury; whence it is evident, therefore, that metallic nitrurets can enter into combination with other bodies. If, then, fulminic acid is a conjugated acid, whose copula is formed by a metallic nitruret, this view would explain why its salts explode whether the base in it be destructible or not, and why not more than half of the metal can be separated from the metallic fulminates as oxide by means of alkali, since only this quantity existed as base in it in combination with the conjugated acid. With respect to the metallic nitruret contained in it, we have, it is true, become acquainted with none other in an isolated state than those which are formed by the reduction of oxides with

ammonia, and which, according to the mode of their preparation, consist of 1 equiv. nitrogen and 3 atoms of metal. It is evident that, although these are principally formed, they are not the sole ones that can exist, and that compounds may likewise be produced in other ways in other proportions. The violence of the detonation appears to indicate that the amount of nitrogen in the supposed copula is probably greater, perhaps in equal equivalents. If now we base our calculation of the composition of fulminic acid on Gay-Lussac and Liebig's analysis, we must double the atomic weight, when we obtain for the hydrated acid the formula $AgN + C^4 NO^3 + HO$. We know that the Ag in the copula may be exchanged for Hg and Zn, and that the water in the formation of salts may be replaced by alkalies, earths and metallic oxides.

In accordance with the new view, we have consequently fulminating acids with three distinct metallic nitrurets,—silver, mercury and zinc, which should be distinguished by separate names, for instance, argento-fulminic acid, hydrargyro-fulminic acid, and zincofulminic acid.—Berzelius, *Jahresbericht*, vol. xxiv. p. 27.

On Phosphuretted Hydrogen. By M. Paul Thenard.

In a former paper* I showed that the inflammability of phosphuretted hydrogen gas was owing to a very small quantity of vapour of a spontaneously inflammable liquid phosphuretted hydrogen, which was easily decomposed into gaseous phosphuretted hydrogen and into solid hydruret of phosphorus.

Having terminated the analysis of the phosphurets of hydrogen and the investigation of their properties, in order to arrive at the theory of their formation, I had still to examine the nature and composition of the phosphuret of lime which I employed, as well as the production of the very various products obtained by treating this phosphuret with water or hydrochloric acid.

1. If some vapour of phosphorus be passed over little balls or thin plates of incandescent lime, an increase of weight, always proportional, is obtained. The lime therefore does not become saturated more at the surface than at the centre, and the combination it forms with the phosphorus is constant.

2. By calculating the increase in weight of the lime after saturation; by observing the quantity of oxygen which unites with the phosphuret of lime in order to convert it into phosphate; lastly, by determining the nature of this phosphate, we find, by three different methods, which reciprocally check each other, that the phosphuret of lime is a combination of 1 equiv. of phosphorus with 2 of lime, $P Ca^2 O^2$.

3. This formula is but the rough expression of the sum of the elements which enter into the phosphuret of lime; it is certain, *à priori*, that they are otherwise combined.

Some chemists have admitted that the phosphuret of lime is a

* Chem. Gaz., p. 486.

combination of phosphate and of phosphuret of calcium; they have assumed that the lime is in part decomposed by combining with the phosphorus; the oxygen uniting with some phosphorus to form phosphoric acid, and afterwards phosphate of lime, and the calcium combining with another quantity of phosphorus to produce phosphuret of calcium. This fact had become certain after a memoir of M. Gay-Lussac on the formation of the alkaline phosphurets and sulphurets; but there was an important point which perhaps had not been sufficiently urged; the nature of the phosphate, and especially of the phosphuret, had not been made evident enough; it had only been generally admitted from analogy that the phosphate was neutral or basic, and that the phosphuret corresponded to the phosphuretted hydrogen gas; it was however essential to determine accurately the composition of the phosphuret of calcium, in order to ascertain the mode of formation of the phosphuretted hydrogens; if it had been known sooner, it is probable that the question of inflammability would not have remained so long in doubt.

It is by taking exact account of the action of hydrochloric acid on the phosphuret of lime, that I became aware of the nature of the phosphate, and of the phosphuret of calcium which compose it.

1. On adding some phosphuret of lime by degrees to concentrated hydrochloric acid, the existing phosphate of lime is dissolved; non-inflammable phosphuretted hydrogen gas, solid phosphuretted hydrogen, and some chloride of calcium are obtained by the decomposition of the phosphuret of calcium. When the reaction is terminated, if the liquor be filtered and ammonia added to it, the whole of the phosphoric acid is precipitated in the state of bone phosphate of lime, which it is easy to collect and weigh.

In this experiment it is impossible that phosphoric acid should form in the presence of the solid phosphuretted hydrogen, and without production of hypophosphorous acid; that which is found must therefore pre-exist in the phosphuret; it originated at the moment of the union of the lime with the phosphorus.

2. It was, however, important to determine the quantities of gaseous and solid phosphuretted hydrogen which are formed when phosphuret of lime is treated with hydrochloric acid. I therefore repeated the preceding experiment; but instead of filtering the liquor, to separate the solid phosphuretted hydrogen, I transformed it into phosphoric acid by the addition of some nitric acid, and then saturated the solution with ammonia, when precisely twice the quantity of bone phosphate was precipitated, as in the first case; which shows that 7 equiv. of phosphuret of lime contain 2 equiv. of phosphorus in the state of phosphoric acid, and 5 in the state of phosphuret of calcium; and that these, under the influence of hydrochloric acid, separate, giving rise to 1 equiv. of solid phosphuretted hydrogen, and 3 of gaseous phosphuretted hydrogen, as if they arose from the partition of 5 equiv. of the liquid phosphuretted hydrogen.

But on applying the laws of the formation of alkaline phosphurets,

it is easy to see that, of the 14 equiv. of lime which exist in 7 equiv. of phosphuret of lime, 10 are decomposed; the oxygen unites with 10 equiv. of phosphorus to form phosphoric acid, and the calcium combines with the phosphorus which remains, producing phosphuret of calcium. Thus the phosphuret of lime is a mixture in definite proportions of 2 equiv. of phosphate of lime and 5 equiv. of phosphuret of calcium, both corresponding to the liquid phosphuret of hydrogen, and not to the gaseous phosphuret of hydrogen:

$$2PO^5\,4CaO + 5PCa^2 = 7PCa^2\,O^2.$$

If we add that the solid phosphuret of hydrogen is transformed, under the influence of water and of an alkali, in the cold into hypophosphite, phosphuretted hydrogen and free hydrogen; also that hydrochloric acid suddenly transforms the liquid phosphuret into phosphuretted hydrogen gas, and into solid phosphuret of hydrogen, it will be easy to explain the varied phænomena which the phosphuret of lime presents in its contact with water and hydrochloric acid.

1. Water and phosphuret of lime first produce some liquid phosphuret of hydrogen and some lime, with scarcely any appearance of hypophosphite; the liquor indeed becomes very alkaline.

2. As the liquid phosphuret of hydrogen is very unstable, especially in the presence of lime, it becomes transformed into spontaneously-inflammable phosphuretted hydrogen gas, and into solid phosphuret of hydrogen.

3. As the action progresses and the quantity of lime increases, the gas becomes gradually less spontaneously inflammable, and contains more and more hydrogen, because the solid phosphuret of hydrogen disappears under the influence of water and of the alkali.

4. From this period, the liquor, which at first contained but little hypophosphite, is very much charged with it; it may be collected by filtering and evaporating.

The phænomena which the phosphuret of lime presents with hydrochloric acid are explained with equal facility.

If this phosphuret be conveyed into concentrated acid, the liquid phosphuret of hydrogen is suddenly decomposed wherever it may form, and transformed into phosphuretted hydrogen gas not spontaneously inflammable, and into solid phosphuret of hydrogen, which is preserved because the medium is acid instead of being alkaline; there is, in such case, neither disengagement of free hydrogen nor formation of hypophosphite.

When the acid is very dilute, the liquid phosphuret of hydrogen is not so quickly decomposed, and the gas given off is spontaneously inflammable. In a word, I think that I am not going too far in saying that all the phænomena known, at least up to the present time, are very satisfactorily explained by the preceding observations. —*Comptes Rendus*, Aug. 5, 1844.

On the Bile. By M. Platner.

The agreement of the results obtained by Dr. Kemp and MM. Theyer and Schlosser in the analysis of the bile, leaves hardly any

doubt that this body possesses a constant composition, and that soda forms an integral part of it. The fact discovered by M. Platner seems to be of a nature to dissipate all doubt which might still exist in this respect.

Some fresh ox-bile is evaporated as nearly as possible to dryness in the water-bath, then treated with absolute alcohol and filtered; the filtered solution is decolorized with charcoal, or if this does not succeed, it is subsequently decolorized with hydrated protoxide of tin, as will be hereafter pointed out; or it is not decolorized at all; the result has always been the same; a further proof that the colouring matter is not essential to the composition of the bile. The solution of the bile, decolorized or not, is placed aside for several days; a small quantity of mucus still separates from it. It is then filtered afresh, and tested with absolute alcohol; if this produces a turbidness in the liquor, the quantity must be augmented, and it must be filtered again. We may then proceed in different ways; either a current of hydrochloric gas is passed into the liquor until it is slightly acid, or a saturated alcoholic solution of oxalic acid, is added to it until no more precipitate forms. The precipitate is separated by filtration, and when hydrochloric acid has been employed, it should be digested with oxide of lead; when, on the contrary, oxalic acid has been employed, its excess is removed by some carbonate of lead. If it be then desired to remove the colour from the bile, and at the same time obtain some of the colouring matter, hydrated protoxide of tin is added to the liquor, treated at first with oxalic acid, and then with some carbonate of lead, after having previously diluted it one-fourth with water, and it is heated to boiling, stirring constantly. The colouring matter combines with the tin and is precipitated, and the liquid becomes yellow; when the whole of the colouring matter has been thrown down, the liquid is separated from the precipitate by filtration; the light green precipitate which remains on the filter, and which in some places is even colourless, is washed with water, transferred into a flask, and agitated several times with alcohol, to which a few drops of sulphuric acid have been added, until the whole of the colouring matter has been removed and the precipitate has become perfectly white. It is then filtered, and to the filtered liquor, which is of a beautiful green colour, a large quantity of water is added, and it is then left quiet for some time. The colouring matter separates in flakes; to unite them the vessel is slightly warmed; it then forms a tolerably compact deposit on the sides, and the supernatant liquid can be decanted. The colouring matter is washed several times with water, and dried in the air, and deprived of fatty matter by digestion with absolute æther. It then forms a green resinous mass, easily pulverized, insoluble in water, but very soluble in alcohol; it is slightly soluble in æther. It is without odour, and has a slightly bitter taste; is insoluble in hydrochloric and sulphuric acids, but dissolves with ease in potash and ammonia, and the green colour is then changed into a yellow. The green becomes pale, and likewise passes into yellow by heat. Heated with potash it disengages ammonia; if this disengagement does not

proceed from some other body, it results that the colouring matter of the bile cannot be identical with chlorophylle, as supposed by M. Berzelius.

A current of sulphuretted hydrogen is now passed through the bile, decolorized or not, and separated from the precipitates by filtration, to free it from the metals (lead and tin) in solution; it is filtered again and placed aside; there then generally separates, if the solution has been diluted with water, a small quantity of choloidic acid, arising from a partial decomposition of the bile; for a small quantity of taurine is formed simultaneously. The solution of the bile is separated from the choloidic acid and evaporated to dryness, towards the end of which operation it should be constantly stirred. The liquid never becomes completely solidified by heat; but it must not be removed from the water-bath before it allows of being drawn out with the glass rod into long filaments, which immediately solidify and break. The capsule is then cooled, and the mass in it reduced to a powder before it can attract moisture. This powder forms a milky solution in water, arising from the choloidic acid in combination with the undecomposed bile. The powder is conveyed into a glass flask, and a quantity of absolute alcohol exactly requisite to dissolve it with the assistance of heat added; generally an equal volume suffices. A large quantity of æther, from 10 to 15 times its volume, is poured into the solution, which is then exposed for several days in a closed vessel to an intense cold. The author has always employed for this operation the cold nights of winter when it froze strongly; for artificial cold presents, in this instance, considerable difficulties. There is then formed at the bottom of the vessel crystals mixed with a yellow non-crystalline mass (choloidic acid); but at the same time some perfectly-colourless white acicular crystals, in radiate groups, appear on the sides of the vessel and in the æther. The æther is decanted, the residue dissolved again in alcohol, and more æther added to it. This operation is repeated several times. The decanted æther is united, absolute æther added to it, and again exposed to cold. A larger quantity of these crystals are then obtained; they are perfectly pure bile, or, according to M. Liebig, bibilate of soda; they have a slightly sweetish, subsequently bitter taste, dissolve with extreme facility in water and in alcohol, deliquesce immediately by mere exposure to air, and can consequently only be preserved under the æther or in their mother-leys. Their solution is neutral, but the deliquesced crystals have a decidedly acid reaction; yet this acid reaction disappears on the addition of water. Their solution is not precipitated by acetate of lead, but it is immediately, and of a white colour, by the subacetate and nitrate of silver. Hydrochloric, sulphuric and nitric acids produce no opakeness in the cold, even when they are concentrated.

Professor Liebig, to whom the author forwarded some of these crystals, found that the acetate of lead precipitated them after previous neutralization of their acid reaction; he moreover observed that their aqueous solution, which is not rendered turbid by the ad-

dition in the cold of hydrochloric acid, becomes opake and deposits oily drops on the application of heat. The addition of water produces a white opakeness, and solidifies them. After removing the hydrochloric acid and pouring water over the oily body, it dissolves entirely, and is precipitated again by hydrochloric acid. This property characterizes bilate of soda (pure bile). Heated with moderately-concentrated sulphuric acid, the solution of the crystals assumes the colour and aspect of old bile; M. Liebig consequently does not doubt that M. Platner has succeeded in obtaining the acid bilate of soda in crystals. If, after having removed the crystals, the æther employed for the crystallization is distilled, a body remains, which after several ebullitions with water behaves absolutely like the biliary resin of M. Gmelin. In the dry state it is brittle, easily pulverized, and leaves no ash on combustion. It is insoluble in water, but very soluble in alcohol. The addition of water separates it in the form of a milky precipitate; the solution reddens litmus-paper strongly, expels carbonic acid from the carbonates of ammonia and soda, and forms with these bases compounds soluble in water. Caustic potash, soda and ammonia likewise dissolve it, but it is insoluble in the carbonate of potash. Concentrated nitric acid dissolves it, with liberation of red vapours, effervescence and considerable elevation of temperature. The lime salts then produce in the solution an opakeness, which is probably owing to the formation of oxalic acid. Concentrated sulphuric acid likewise dissolves it, although slowly, but with a dark red colour, almost black.

The author concludes with some observations on the colouring matter of the bile. The bile, as is well known, gradually becomes green by the action of acids, if the access of air be not prevented; but the change of colour of the bile is instantly effected by nitric acid; it first becomes green, then blue, violet, and lastly yellow; subsequently the nitric acid destroys the colouring matter. M. Platner has moreover observed that the simple access of air gradually produces the same changes of colour. If, in fact, an alcoholic solution of the bile be exposed for some time to the air, it first becomes green, but then passes gradually to red. There can be no doubt, consequently, that these changes of colour are due to a progressive oxidation of the colouring matter. That which M. Berzelius obtained from bile by means of barytes contained no nitrogen; but that which the author prepared in the manner above described is nitrogenous. This subject requires, therefore, further investigation. —Liebig's *Annalen*, vol. l. p. 105.

On the Formation of a new Oxychloride of Mercury.
By M. Ch. Roucher.

The action of hydrochloric acid on the binoxide of mercury would appear, at first sight, simply to consist in the production of some bichloride; but a fuller examination has led me to discover that whenever an excess of the oxide of mercury is in the presence of the bichloride, the two bodies combine and form several com-

pounds very different in appearance. Amongst these we find, in the first place, the black oxychloride, recently described by M. Thaulow, 2HgO, HgCl; then a yellowish-white crystalline body, which is always deposited by the mercurial liquor at the same time as the bichloride, with which its appearance, as well as its mode of origin, have often caused it to be confounded.

The new compound always separates, but in quantities which vary according to circumstances, from an aqueous solution of the bichloride which has been boiled over an excess of oxide, and left to crystallize by cooling. The first deposit which takes place in the filtered liquor is a confused mixture of differently-coloured oxychlorides, and without any defined form; these are nearly wholly precipitated at a temperature above 140°. The liquid being then decanted, if it is not too concentrated, exhibits, between 122° and 104°, in the midst of the crystals of bichloride, a number of more minute crystals, isolated, less transparent, and of a totally different form from the first; they are oblique prisms, with truncated rhomboidal base; in mass they are of a white colour, with a slight tint of straw-yellow. They are very easily separated from the crystals of the bichloride, with which they are always mixed, by means of absolute alcohol, which dissolves the latter, leaving the oxychloride intact from its insolubility in this medium.

The composition of this body is represented by the formula HgO, 2HgCl.

Besides this oxychloride, there is sometimes found in the same liquor another compound, which is likewise white and crystalline, but in the form of very light and brilliant nacreous laminæ; they are in so far peculiar that they are decomposed in every kind of solvent except the liquid in which they formed. Absolute alcohol, however, changes them with less rapidity than the rest, and reduces them to the composition of the first white crystalline oxychloride, destroying their form, which strongly leads to the suspicion that they contain still more bichloride than the latter.—*Comptes Rendus*, Oct. 14, 1844.

ANALYTICAL CHEMISTRY.

On the Use of Sulphurous Acid in Analysis, as proposed by Berthier. *By* Dr. H. Böttinger.

Dr. H. Böttinger, under the guidance of Dr. Will, has examined practically the methods proposed by Berthier * for the separation of several metallic oxides, by means of sulphurous acid or alkaline sulphites; we give the results, omitting the details of analyses, &c., which appear to have been conducted with great care.

Alumina, Glucina, and their separation.—He completely confirms the account given by Berthier of the behaviour of alumina

* See Chemical Gazette, vol. i. pp. 289–318.

towards this reagent; he did not find the precipitated alumina quite free from sulphurous acid, however, even after very long boiling. Hydrate of glucina he also finds to be easily soluble in sulphurous acid, as stated by Berthier, and not precipitated by continued boiling. But although the behaviour of these earths individually towards sulphurous acid appears favourable to their separation, still it does not succeed; as it would appear from the author's experiments that a portion of the glucina is always precipitated in company with the alumina, and is not redissolved by protracted ebullition. The usual method of separating these earths by carbonate of ammonia is therefore preferable.

Oxide of Chromium is not precipitated by sulphite of ammonia; but if alum is mixed with its solution, the oxide of chromium is thrown down, together with the alumina, by boiling with sulphite of ammonia.

Separation of Alumina from Iron.—When a sufficient quantity of sulphite of ammonia is added to a solution of both oxides, and the whole boiled until the odour of sulphurous acid is no longer perceptible, the alumina is completely precipitated free from oxide of iron, as Berthier states. The access of air must be prevented as much as possible. The author, however, found it impossible so to separate the solution of protosulphate of iron from the precipitated alumina as to prevent its being coloured by sesquioxide of iron, or obtained perfectly free from it.

Separation of Uranium from Nickel, Cobalt, Zinc and Iron.—Two causes occur to prevent the separation of uranium from these metals; one owing to the easy oxidation of the protoxide of iron, which prevents the uranium from being obtained free from sesquioxide, and the other metals being partially precipitated by the sulphite; and the other, in consequence of the oxide of uranium not being entirely precipitated by sulphite of ammonia, even when a large excess of the precipitant is added, and the boiling continued very long.

Separation of Tin from Antimony.—The method by which Berthier proposes to separate these two metals, viz. by mixing the solution of both metals in hydrochloric acid with tartaric acid, and boiling with sulphite of ammonia until the tin is precipitated, does not succeed, as the tin is not completely precipitated when tartaric acid is present, and without it the antimony is partially precipitated.

Separation of Copper from Zinc, Cobalt, Nickel, Manganese and Iron.—As oxide of zinc is precipitated with difficulty, and even after long boiling only partially; and as, on the other hand, the greater part of the copper is instantly precipitated, this method might be employed to estimate approximatively the quantities of these two metals, although it possesses no particular advantage over the method generally used. In exact analysis, however, it is inadmissible. For the separation of copper from iron, manganese, nickel and cobalt, it is impracticable, for reasons mentioned under the head of uranium, and as copper moreover is not completely precipitated by sulphite of ammonia.—*Ann. der Chem. und Pharm.* for Sept. 1844.

PHARMACOLOGY.

On Variolaria amara, *Ach.** *By* C. A. Müller.

According to a recent notice by M. Filhol, he could not succeed in obtaining pikrolichenine, which was first described by Alms, from the *Variolaria amara*. This induces me to suspect that some other lichen of this genus, and not *Variolaria amara*, has been examined, since I have verified the statement of Alms, with reference to that species, in every respect.

The preparation of the pikrolichenine is not at all connected with any difficulty. It crystallizes in a few days from the extract, obtained by digesting the powdered lichen with alcohol of 0·889 to 0·863 spec. grav., and removal of the spirit by distillation, evaporated nearly to the consistence of a syrup. Since it is only soluble in small quantity in cold alcohol of 0·912 spec. grav., the resin is readily washed from the crystals with a little spirit. If a solution of potash be used for this purpose, as recommended by Alms, there is danger, if it be too concentrated, of losing the separated pikrolichenine, as it dissolves in it with a red colour. It is purified by repeated solution in alcohol. It is however difficult to obtain it perfectly pure, as a trace of a greenish resin adheres to it very tenaciously.

The lichen also contains a bitter dark green resin, which in its properties is very analogous to pikrolichenine. It almost resembles aloes in colour, dissolves in æther, absolute alcohol, and spirit of 0·912 to 0·889 spec. grav., with a green colour, but not in oil of turpentine. On dissolving it in a solution of potash, it smells of aniseed, and the liquid acquires, after some time, a deep red colour, and subsequently deposits a brownish-red body.

I found in 100 parts of the lichen—

Pikrolichenine	2·395
Brownish yellow resin extracted by æther	0·677
Dark green bitter resin	1·979
Chlorophylle	4·114
Mucous sugar	1·960
Aqueous bitter extractive substance	3·645
Oxalic acid	3·208
Lime	2·521
Silica	1·770
Iron	traces
Fibre and substances not examined	77·731

If there were not already so many bitter agents in the Materia Medica, this lichen, which occurs in such quantity in our forests, would certainly merit every attention. According to Cassebeers's experiments, it acts in fevers like bark.

The best form for the employment of this remedy would be the tincture, prepared by digesting the dried and pulverized lichen with

* See M. Dassier's remarks on this subject, p. 426.

alcohol of 0·863 spec. grav., of which three times the quantity of the lichen should be taken. The greater portion of the bitter substances is contained in this liquid.—*Pharm. Cent. Blatt.*, Nov. 2, 1844.

On the Demerara Pink-root, or Spigelia Anthelmia*. By Dr. George R. Bonyun†.

The indigenous species of pink-root, which is in great repute among the labourers of British Guiana, particularly those residing on the banks of the rivers, has not as yet, I believe, in this colony been sufficiently brought to the notice of medical men, nor its relation to the *Spigelia marilandica*, or officinal pink-root, determined. This herb, which grows in great abundance on the west and Arabian coasts, and on the banks of the rivers, is identical with that described by Patrick Browne, anno 1756, p. 156, in his 'Civil and Natural History of Jamaica,' as "Anthelmintia or wormwood." He there says, "This vegetable has been long in use among the Negroes and Indians, who were the first acquainted with its virtues, and takes its present denomination from its peculiar efficacy in destroying worms, which I dare affirm, from a great number of successful experiments, it does in so extraordinary a manner, that no other simple can be of equal efficacy in any other disease, as this is in those which proceed from these insects, especially when attended with fever or convulsions." Griffith Hughes, in his 'Natural History of Barbados,' 1750, p. 230, likewise mentions this plant as a powerful anthelmintic, under the name of "Loggerhead weed." Fusée Aublet, 'Hist. des Plantes de la Guiane Française,' vol. i. p. 126, calls it, from Margraave and Plumier (1703), "Arapabaca," and gives the French name by which it is generally known through the French islands, "La Brinvilliers," after the infamous marquise de Brinvilliers, who, in conjunction with her lover St. Croix, poisoned so many people in France in the reign of Louis XIV. The 'Icones Plantarum Medicinalium,' Nuremburg, 1799, gives a plate of *Spigelia anthelmintica*, and Linnæus, 'Species Plantarum,' anno 1762, tom. i. p. 213, describes the plant; but no mention is made in either of these works of the Maryland species. Pereira, 'Elements of Materia Medica,' 1842, vol. ii. p. 1288, describes the *Spigelia anthelmintica* as possessing medicinal qualities similar to the Maryland species, quoting from Browne; and Nees ab Esenbeck, 'Handbuch der Medicinisch-pharmaceutischen Botanik,' 1831, vol. ii. p. 654, gives a long description of both species, giving however a preference to the Maryland species, "as being more used in North America."

I have been thus particular in giving an account of the history of our indigenous species in consequence of being desirous to show,

* *S.* Caule herbaceo ramoso, foliis oblongis utrinque attenuatis, summis quaternis, racemis spicatis staminibus corolla brevioribus.—*Sprengel*, vol. i. p. 584.

† Read before the Agricultural and Commercial Society of British Guiana, 9th Sept. 1844.

that the vermifuge *Spigelia*, first brought to the notice of Europeans, was the one indigenous to the islands and continent of South America, and not the Maryland species, which became known afterwards, and has been since substituted for our species. The first mention of *Spigelia marilandica*, Pereira states, was in 1740, whilst the *Spigelia anthelmintica* was noticed by Plumier, 'Nova Plant. American.' gen. 11, in 1703, under the name of Arapabaca. The *Spigelia marilandica* is collected, according to Thompson, Pereira and others, by the Creek and Cherokee Indians, and sold to the American merchants. As it is scarcely used in England, a quantity only sufficient to supply the West Indies is imported, and that generally in a bad state. Pereira says, vol. ii. p. 1286, "Owing to the imperfect manner in which the plant is dried, it seldom happens that packages of it reach the market free from dirt and mouldiness."

The quantity of Maryland pink-root imported here may not amount to much; but it appears evident, if we can procure, in our immediate vicinity, without much labour, an article superior both in regard to freshness and activity, that it is worth while bringing it to the notice of poor people, who may turn a penny or two by collecting and drying the plant. To the medical men in the colony, who are in the habit of using a mouldy, uncertain remedy, sometimes in enormously bulky and disagreeable doses, as a *substitute* for the fresh plant within their immediate reach, it is a matter of some importance.

With regard to the great efficacy of the plant, the testimony of Browne, a learned physician and excellent botanist above quoted, and the experience of the common people (by no means a despicable criterion) ought to be relied on. The late Mr. J. D. Paterson of Christianburg, a gentleman of remarkable powers of observation and strong intelligence, told me shortly before his death, that he was in the habit of administering the Demerara pink-root, in decoction, in the proportion of from two to three fresh leaves for a dose, and that the effect was much more certain and marked than that produced by the pink-root of the shops, in thirty or forty grain doses. I have likewise lately been informed of several cases in which the decoction of the fresh leaves of our species was efficacious when the Maryland pink-root failed.

I need not lengthen these few remarks, as my object is merely to suggest to medical practitioners the superiority of the fresh or recently dried *Spigelia anthelmia* to the broken and mouldy *Spigelia marilandica* brought into this colony from a great distance, and to introduce, however insignificant it may be, a new source of industry to the poor. The preparation of the plant for sale is very simple: it must be pulled up by the roots in a green state, and the seeds stripped off; it is then to be carefully cleaned, dried in the sun, and packed in bundles.

CHEMICAL PREPARATIONS.

On the Preparation of Medicinal Prussic Acid, and on the Action of Sulphuric Acid upon Ferrocyanide of Potassium. *By* M. Thaulow.

The following are the results of the author's investigation, which differ considerably from Liebig's view, that in the action of sulphuric acid upon the ferrocyanide of potassium, at first only ferrocyanic acid is given off, which is then decomposed into prussic acid and white cyanide of iron containing potassium, which becomes blue on exposure to the air by the absorption of oxygen, and that four-fifths of all the prussic acid contained in the salt is the maximum which can be obtained.

The principal cause of the constant difference in the amount of officinal prussic acid is owing to the *slow* distillation, which favours the spontaneous decomposition of the acid during the process. If the distillation is carried on rapidly, a maximum of prussic acid, which amounts exactly to three-fourths of the prussic acid of the cyanide of potassium, is constantly obtained, while the cyanide of iron remains wholly undecomposed.

The quantity of the sulphuric acid is without any influence on this result, so long as it does not amount to *less* than three-fourths of an equivalent for each equivalent of cyanide of potassium. In the decomposition a green pulverulent body separates at 135° on heating the cold mixture gradually, which is a cyanide of iron containing potash, becoming gradually blue by contact with sulphuric acid, without any absorption of oxygen. The evolution of prussic acid, however, only begins at 219° to 221°, after the liquid has begun to boil. Before the liquid in the retort becomes thick, the evolution of prussic acid has terminated. We have then a distillate, which contains, besides prussic acid, always some ammonia (while some formic acid is contained in the water which passes over during the distillation), in the retort an acid liquid perfectly free from iron, and the above-mentioned green precipitate, which contains the whole of the iron. At all events, therefore, the yellow prussiate is first decomposed into cyanide of potassium and cyanide of iron before the evolution of prussic acid begins, and the ammonia and formic acid proceed from the decomposition of the cyanide of potassium on boiling and of the prussic acid in contact with sulphuric acid. But the cyanide of ammonium is the cause of the instability of the prussic acid, which is avoided by the presence of a mineral acid. In accordance with these observations, the following recipe might be recommended for the preparation of a medicinal prussic acid of uniform strength:—153 grs. of pure ferrocyanide of potassium, 76 grs. concentrated sulphuric acid*, and 4 oz. of water are mixed in a retort; this connected with a cooling tube so as to form an obtuse angle, and the latter with a recipient containing 1 oz. of distilled water. The retort is now heated in a chloride of calcium bath of such con-

* A slight excess, on account of the varying strength of the so-called concentrated sulphuric acid.

centration that the boiling-point may rise to about 266°; it is heated to 257°, and the operation carried on at this temperature from 15 to 20 minutes, then discontinued, the product brought by the addition of water to 3 oz. 6 drms. 36 grs., and from 3 to 4 drops of sulphuric acid added to it. This acid contains 1½ per cent. of anhydrous acid, and 5 drops of it are equal to 2 drops of the *Acid. hydrocyan. alcoholis.* of the Norwegian Pharmacopœia. The following are the experiments and observations of the author upon which the above formula is based:—

The experiments were made with pure ferrocyanide of potassium and with pure sulphuric acid of 1·82 spec. grav. They were executed with the assistance of Liebig's cooling apparatus, with which a tubulated glass retort was connected in such a manner that the neck of the retort formed with the cooling apparatus an angle of about 145°. The retort was kept floating in a vessel filled with a boiling solution of chloride of calcium, and a beaker glass with a dilute solution of silver served as recipient; the lower extremity of the cooling tube being constantly kept some lines beneath the surface of the solution. As, on the immediate decomposition of the prussic acid passing over, well-defined currents of white cyanide of silver formed, it was possible to follow the course of the operation accurately. At first 51 grs. of the yellow salt (containing 19·7 anhydrous prussic acid) were employed, and 26 grs. sulphuric acid of 1·82 spec. grav. 9·62 grs. anhydrous prussic acid were obtained.

For the following experiments so much sulphuric acid was taken as was exactly required to convert the bases into bisulphates. Three distillations were made with this quantity, the operation being always continued as long as cyanide of silver formed in the recipient. The quantity of anhydrous prussic acid amounted to 9·52, 9·73, and 9·19 grs. The amount of prussic acid, however, only approaches to constancy when the distillation is not continued until the residue is perfectly dry, but is interrupted as soon as the formation of cyanide of silver in the recipient has ceased. If the sulphuric acid be diluted with from 1½ to 2 oz. of water, and the distillation rapidly carried on without interruption, the mixture in the retort is still perfectly fluid when the production of cyanide of silver has ceased. If the liquid in the retort be filtered from the sediment, not a trace of iron or cyanogen is found in it, and the sediment itself retains its *green* colour, which it acquired on the first action of the sulphuric acid.

Another experiment, which was likewise performed with the same mixture of acid and salt, but in which the distillation was carried on until the residue was dry, and the chloride of calcium bath kept boiling for some time afterwards (15 minutes), gave somewhat different results; for the first ten minutes the recipient was still kept in connexion with the cooling apparatus, the temperature of the saline bath, which during the first period of the distillation had not exceeded 257°, being now raised to 275°, and only for the last 5 minutes the recipient was changed for a beaker glass with pure water, while the chloride of calcium bath was allowed to reach a temperature of 284°. In this experiment the quantity of anhydrous

prussic acid amounted to 10·21 grs.; but the water of the receiving-glass likewise contained, besides much free sulphuric acid, some cyanogen, and another body with a penetrating odour, respecting which Thaulow is not able to prove with certainty whether it arose from formic acid, or from sulphurous acid, or perhaps from a mixture of the two.

The residue in the retort had, immediately on being removed from the fire, a porous appearance, and a colour exactly similar to that of the ammonio-sulphate of copper. 2 oz. of water were added to it, after which it was perfectly washed, when it afforded 18 grs. of a body of a most beautiful blue colour, which however had no resemblance with that of prussian blue, but appeared rather like that of indigo. The water filtered from the blue residue was perfectly clear and colourless, but had a strong acid reaction. The author was accidentally prevented from ascertaining immediately its precise amount; and as he was about to commence this examination 3 hours later, it had become yellow, and resembled a concentrated solution of the prussiate of potash. The solution was now exposed to the direct action of the light of the sun; in the course of a few minutes a faint light blue cloud began as it were to form in the centre of the liquid, which quickly increased in volume, and before one hour had elapsed the liquid had become opake, and now exhibited the most beautiful tints of blue and violet, through green to brownish-red, according as the glass was held towards transmitted or reflected light. After it had stood quiet for 2 days, a small quantity of a dark blue precipitate had formed, and it now afforded a clear liquid on filtration.

The sulphuric acid in this liquid was accurately saturated with carbonate of potash; no iron was found by this means in the neutral solution formed, but, on the contrary, the liquid itself produced precipitates; for instance, in salts of copper a dirty grayish-brown, in persalts of iron a beautiful green, in protosalts of iron a dirty green, which did not change by standing; in salts of silver a dirty brown precipitate, which on being treated with nitric acid disengaged carbonic acid and left behind a heavier dirty yellow powder. It produced no precipitate in salts of zinc, but on the other hand it produced, after decomposition with nitrate of barytes, a precipitate in salts of lead, which was insoluble in nitric acid.

In these experiments the author observed that cyanide of silver is somewhat soluble in dilute nitric acid. Now since, at the formation of cyanide of silver from the nitrate, some free nitric acid must always be formed, it was held to be requisite to test the liquid filtered from the cyanide of silver. It never contained cyanide of silver, but it constantly afforded on evaporation a small residue of a salt of ammonia. The ammonia might possibly have resulted from the action of an hydracid on the nitrate, in the same manner as it is formed on the decomposition of nitrates by sulphuretted hydrogen; but the following experiments render it more probable that it arises from a decomposition of cyanide of potassium and prussic acid.

If we calculate how much of the sulphuric acid of 1·82 spec. grav.

employed in the experiments above described is requisite to form a neutral salt with the amount of potash in 51 grs. of the yellow prussiate, 25·4 grs. will be found to be necessary. Two experiments were now made with 27·83 grs., and two others with 25·4 grs. of sulphuric acid of 1·82 spec. grav. 27·83 are to 25·4 grs. as 26 grs. of "mono"-hydrated sulphuric acid are to the 23·738 grs. of this acid, required for the perfect neutralization of the potassium in the yellow prussiate.

In all these experiments ammonia was constantly found in the liquid from which the cyanide of silver had been filtered, and the excess of silver removed by hydrochloric acid. They were modified in the following manner:—The sulphuric acid was diluted with $1\frac{1}{2}$ oz. of water, a thermometer inserted into the tubulated retort, and arranged so that the operation could be immediately interrupted as soon as the formation in the recipient of cyanide of silver had ceased*.

In the first experiment, with 27·83 grs., the quantity of prussic acid in the distillate was determined immediately: and it will be seen in the following why this one determination, in which 47·33 grs. cyanide of silver, or 9·65 anhydrous prussic acid, were obtained, must be regarded as sufficient to prove that 27·83 grs. sulphuric acid of 1·82 spec. grav., and 26 grs. of the monohydrated sulphuric acid, are not necessary; or, in other words, that a slight excess of sulphuric acid is by no means requisite in order to obtain the greatest amount of prussic acid. In the other experiment of distillation with 27·83 grs., and in the first experiment with 25·4 grs., only a very inconsiderable quantity of sulphuric acid was found in the liquid separated from the silver salts, after the excess of hydrochloric acid in it had been slightly supersaturated with pure carbonate of soda, and subsequently concentrated by evaporation.

A fuller explanation of the mode of decomposition of the cyanide of potassium must be sought for in the analysis of the residue remaining in the retort; and with this view we will first consider the experiment of distillation made with 27·83 grs. sulphuric acid. Immediately after the operation was completed, the still-fluid green residue was treated with a little water, then filtered, and washed without interruption until nothing further was removed. An unaltered green powder remained, the weight of which, after desiccation at 212°, amounted to 18·15 grs. The liquid obtained with the water first added was clear and colourless, and possessed an acid reaction, which arose from free acid, since on the addition of a little carbonate of potash a faint effervescence ensued. Neither cyanogen nor iron were found in this liquid after neutralization with carbonate of potash. But although it cannot be admitted that some undecomposed ferrocyanide of potassium could be present in a previously *heated acid* and clear liquid, and although this liquid produced

* It will perhaps not be unnecessary to observe, that the presence of ammonia was asertained in experiments with four times the quantity of the stated portions of material. But for the sake of rendering it intelligible at a glance, all the numbers have been reduced for 51 grs. ferrocyanide of potassium.

after neutralization not a trace of prussian blue with protosalts of iron, it was finally evaporated to dryness in the water-bath, since, as is well known, the usual tests for iron do not act on this body in the dissolved ferrocyanide of potassium. Some of the saline mass was ignited, and further treated in the usual manner, without any trace of iron being detectable. The evaporation of the liquid was performed in a water-bath, in order to be able to search at the same time for ammonia in this liquid. With this view a few small pieces of hydrate of potash were mixed at the bottom of a test-tube with the remainder of the evaporated saline mass, and then slightly moistened with water. The heat produced by the action of the water on the potash was sufficient to produce the desired effect, and it was easy to observe vapours distinctly ascending from the glass rod, which had been moistened with dilute muriatic acid and held over it. In the other experiments with 27·83 and 25·4 grs., *the same* result was obtained with respect to cyanogen, iron and ammonia.

If we look at the results in so far as they relate to the quantity of anhydrous prussic acid obtained, it is found to amount on an average to 9·54 grs., which contain 9·13 grs. cyanogen. But the cyanide of potassium in 51 grs. of ferroprussiate of potash contains 12·696 of cyanogen and 18·926 potassium; and it is consequently evident that, in the action of sulphuric acid on the ferrocyanide of potassium, both on the employment of exactly the theoretical proportion as well as of any larger amount of acid, three-fourths of the cyanide of potassium constantly give their cyanogen for the formation of prussic acid. Setting out from the constant amount of cyanogen in the distillate mentioned above, in order to determine from it the quantity of the sulphuric acid employed, and which would be requisite to produce the same quantity of cyanide of silver in a direct and complete decomposition of a metallic cyanide, it was found to be 18·4 grs. A fresh experiment was performed with this quantity, and it was surprising that 47·45 grs. of cyanide of silver were obtained, a quantity which agrees as exactly with the calculation as can be expected in operations of this kind.

The behaviour of the residue in the retort was just as remarkable; the washed green sediment weighed 18·09 grs., differing therefore but little from the quantity previously obtained. The liquid filtered from this sediment had an acid reaction, without however producing the slightest effervescence in a solution of carbonate of potash; and on examining it for cyanogen and iron, a proportionately large amount of cyanogen was found, but only a trace of iron.

In order to ascertain accurately the action of sulphuric acid on the yellow prussiate of potash, a thermometer, as above stated, was placed, in some experiments, in the retort. A dilute sulphuric acid produces, as is well known, in a solution of ferrocyanide of potassium, no perceptible change in the cold; and in the experiments here described, the cold, clear mixture was gradually heated by means of a chloride of calcium bath. At about 104° Fahr. the mixture began to grow turbid, and when the temperature had increased to 140° a green pulverulent body was distinctly seen to separate. As the tem-

perature gradually rose, the quantity of this green powder likewise increased; *but no cyanide of silver formed in the recipient before the mixture had attained a temperature of from* 219° to 221°. If we, moreover, add, that in a separate experiment, suddenly discontinued when the temperature had reached to about 215°, the green powder contained just as little potash as the other sediments, to which we shall subsequently return, no further proof appears to be requisite of the partial pre-existence of the cyanide of potassium in the heated mixture; and in this explanation we find a sure guide to the discovery of the source of the ammonia.

With the method and apparatus above described, Thaulow had not the least reason for keeping exactly to the usual order, *fiat distillatio leni calore*, which would have necessarily rendered the operation somewhat tedious. On the contrary, the considerable number of experiments rendered a quick process desirable; and if we compare these results with those generally obtained, in relation to the strength of the acid, the advantage of a rapid execution of the experiment is very striking.

Three experiments were now made with 26 grs., following more closely the above directions. In the first, the formation of cyanide of silver lasted 3½ hours, and its quantity amounted to 43 grs.; in the second, 41·55 grs. cyanide of silver were obtained in a distillation carried on for 3 hours; and in the third experiment the quantity of cyanide of silver amounted to 40·63 grs., while its formation ceased only after 2 hours 24 minutes.

A fourth experiment was made, to ascertain the minimum of time required for the complete distillation of the prussic acid. When the mixture in the retort had begun to boil violently at 226°, the chloride of calcium bath indicating a temperature of 268°, the greater portion of the prussic acid had distilled over in the course of 3 minutes. The cyanide of silver appeared still to increase in the glass up to the 11th minute; but what passed over between this and the 15th minute was so inconsiderable, that it would not have had the least influence whether subtracted from or added to the quantity of anhydrous prussic acid in the distillate. The weight of the cyanide of silver amounted in this experiment to 48 grs.

With respect to the green residue (which has great resemblance to the green cyanide of iron described by Pelouze, as well as to the green substance which is obtained on heating fragments of prussian blue, and digesting the ignited mass with dilute nitric acid), the constancy in its colour and weight on the employment of sulphuric acid in larger or smaller quantity, if the minimum be not under 18·4 grs., and if the distillation be discontinued as soon as the formation of cyanide of silver in the receiver ceases, has already been noticed. Its colour is *green* from *beginning* to *end*, if the sediment be immediately washed on the termination of the operation; it is of a beautiful bright tint, a little darker than Scheele's green. In the first experiments, which were undertaken with a view of determining the absolute quantity of the prussic acid in the distillate, the tint of the residue was at each time different. Thaulow found this to be

owing to the length of time during which the acid liquid, which formed on adding water to the residue in the retort, remained in contact with the insoluble powder; and by effecting a separation of the acid liquid and the subsequent washing of the powder in various intervals from the immediate washing after distillation to after the lapse of 24 hours, he obtained six perfectly distinct tints, from light green to perfect prussian blue. If the green colour be called No. 1, and the blue No. 6, the intermediate numbers represent the corresponding tints.

In order to ascertain at present how far the supposed absorption of oxygen might cause the successive transition of the originally green colour to the tint of prussian blue, the following experiments were made:—Some of the dry green powder was mixed with water, and exposed for several days in an open glass; if the change depended solely on the absorption of oxygen, it should have happened in the present case just as much as before, but the colour remained unaltered. The admixture of some solution of cyanide of potassium produced no other result; but on the addition of some dilute sulphuric acid a change of colour took place, which in the course of 24 hours resembled prussian blue.

To ascertain whether the presence of sulphuric acid might induce an absorption of oxygen from the air, some of the green powder was mixed in a closed flask with distilled water, which had long boiled; a small glass bulb, with a long thin neck, was filled with sulphuric acid, sealed, and conveyed into the flask. Two apertures in the cork of the flask were provided with tightly-fitting tubes, one of which extended below the surface of the mixture, and the parts projecting out of the flask were both drawn out over a spirit-lamp, at a short distance from their extremities. A current of hydrogen gas was now passed through the longer tube, and when the whole of the atmospheric air had been expelled both the tubes were sealed at the places drawn out; after this the long neck of the glass bulb was broken by shaking the flask, and in this manner the sulphuric acid brought into contact with the powder; on the next morning the powder had become blue. This experiment therefore seems to prove that the blue change of colour is not owing to an absorption of oxygen from the atmosphere, but that it is produced by the action of the sulphuric acid. The author however confesses that he has not yet been able to find any perfectly satisfactory explanation.

With respect to the chemical constitution of this green residue, it may be observed, in the first place, that its quantity remained the same in all the distillations in which it retained the green colour, or in other words, in which it was washed immediately after the distillation, viz. on an average 18 grs., and that in one only of these experiments, in which the weight was ascertained, a trace of undecomposed ferrocyanide of potassium occurred in the liquid filtered from the sediment. It is evident therefore that the whole amount of iron from 51 grs. of the yellow prussiate is found in this green residue. To ascertain whether it also contained potash, 30 grs. were ignited, and further treated in the usual manner. The *presence* of potash

was proved; but although the absolute weight of the chloride of potassium obtained was not determined, the quantity seemed to be proportionally very inconsiderable.

The quantity of iron in 51 grs. of the yellow prussiate amounts to 6·553 grs., which combine with 6·35 grs. cyanogen to form 12·9 grs. protocyanide of iron. Thaulow was induced, from some observations and calculations, to suspect the presence of chemically combined water in the protocyanide of iron obtained; and on heating gradually 36·5 grs. of the dry powder in a suitable apparatus, he noticed the deposition of a considerable quantity of moisture on the cold portion of the apparatus. The temperature was not increased when the globules of water had begun to deposit; they had no reaction. The powder had acquired a pale grayish-yellow appearance, and had lost 8·55 grs. in weight by this operation. This amounts to 3 grs. for 12·9 grs., and on deducting the whole sum from 18 grs., 2·1 grs. remain for the cyanide of potassium. The smallest quantity of cyanide of potassium which can combine in chemical proportions with 12·9 cyanide of iron is 15·65 grs.

It is remarkable that the amount of water found is only 0·38 grs., too small to form with 12·9 protocyanide of iron, hydrocyanic acid, and protoxide of iron. This circumstance induced the author to heat some dry prussian blue in the same manner. It likewise afforded water, and the colour became so much altered that it could not be distinguished from No. 4 of the above-mentioned series of tints. From this it appears that the combinations of iron with cyanogen form hydrates, and that they, like the hydrated oxide of copper, owe their beautiful colour solely to their hydrate water.—*Journ. für Prakt. Chem.*, xxxi. p. 234.

Preparation of Iodide of Potassium. *By* C. Frederking.

30 oz. of iodine are treated in a cast iron-caldron with 15 lbs. of rain water, and gradually 15 oz., or indeed so much iron filings added until the liquid has become clear. The decanted liquor, together with the wash-water, is mixed in a bottle with 10 oz. of iodine, and in this manner a solution of protoperiodide of iron obtained. Upon this so much solution of carbonate of potash is added to it in a spacious vessel until a filtered sample scarcely exhibits the presence of iron; a small portion of the iodide of iron is left undecomposed. The precipitate of protoperoxide of iron is dried in the vessel after removal of the liquid, that it may be more easily washed. The liquid is evaporated in an iron cauldron to dryness, and then melted in it to destroy any iodide of iron that it may still contain. The salt is then dissolved in 8 lbs. of distilled water, the solution filtered, and the iodide of potassium evaporated slowly to crystallization in a porcelain basin. Beautiful large crystals are obtained. The last portions of the liquor are likewise *perfectly neutral*, and may be evaporated to dryness. If a small portion of the iodide of iron be not left undecomposed on precipitating the iron with carbonate of potash, the salt does not require to be fused; but then the last

mother-ley from the crystallization of the iodide of potassium is alkaline.

With 40 oz. of iodine I obtained, in three several experiments, 50 oz., 49 oz. 4 drms., and 50 oz. 4 drms. of neutral iodide of potassium.—*Archiv der Pharm.* for Oct. 1844.

PATENT.

Patent granted to C. Townend, Manchester, *for an improved Preparation for purifying and preventing Mildew in Cotton Fabrics.*

This invention is intended to be applied chiefly to fustian cloths, although it is also applicable to other cotton fabrics; it consists in rendering the fabrics repellent to water and mildew, and preventing any unpleasant smell, by steeping them in, or passing them through, the solutions hereafter described.

As the general practice of dyers is to mix their solutions with reference to the weight of the cloth, or other material, to be immersed therein, and without regard to its length or width, the patentee describes his process upon this plan; the quantities mentioned being calculated for fabrics of which a piece 60 yards long and 27 inches wide will weigh 40 lbs.

To prepare a solution in which the fabrics are to be immersed, the patentee proceeds in the following manner:—20 lbs. of calcined British gum are mixed with 8 gallons of cold water, in a suitable vessel or vat, until fine and pasty; then 10 lbs. of palm or white soap are dissolved in 8 gallons of boiling water, in another vessel, and this solution is added to the former, together with 1 pint of log-wood liquor, and the whole is boiled up together; 3 lbs. of rock alum, dissolved in 1 gallon of water, are then added, and the mixture, after boiling for a few minutes, is ready for use. The cloth or fabric (having been previously prepared and dyed in the ordinary way) is steeped in, or passed through, the above mixture or solution, in the usual manner of stiffening and drying cotton fabrics.

Sometimes the patentee uses two solutions in succession; one of which is formed by boiling 6 lbs. of sulphate of zinc in 9 gallons of water, and when cold drawing off the clear solution; the other is made by dissolving 20 lbs. of calcined British gum in 8 gallons of cold water, and 10 lbs. of palm or white soap in 8 gallons of boiling water, then mixing these two solutions, and after adding a quarter of an ounce of pearlash bringing them up to a boiling heat. The cloth or fabrics are first steeped in or passed through the zinc solution, and immediately afterwards steeped in or passed through the other solution.—Sealed March 6, 1844.

THE CHEMICAL GAZETTE.

No. LII.—December 16, 1844.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Mellon and its Compounds. *By* Prof. J. Liebig.

Völckel, in his recent investigations respecting the decompositions of the sulphocyanides at a high temperature, arrived at the result that Liebig's mellon did not exist as a constant body. This has induced Liebig to recapitulate, in the first place, the results hitherto obtained on this subject, with a special attention to Gmelin's researches on the mellonide of potassium and hydromellonic acid, and then to communicate a series of new experiments proving the independent existence of mellon and its compounds.

Preparation of the Mellonide of Potassium.—a. Add to fusing sulphocyanide of potassium about one-fifth in weight of so-called impure mellon (the residue from the decomposition of the yellow sulphocyanogen). Sulphuret of carbon and sulphur are liberated with effervescence, and a brown mass, soluble in water, is obtained, from which solution mellonide of potassium crystallizes. The impure mellon decomposes, in this case, the sulphocyanide of potassium into mellonide of potassium and so-called sulphocyanogen; this is decomposed at a high temperature into sulphur, sulphuret of carbon and mellon; the latter decomposes a fresh quantity of sulphocyanide of potassium, and so on.

b. A mixture of 3 parts of sulphate of iron and 2 parts sulphate of copper is precipitated with sulphocyanide of potassium, the precipitate washed first with dilute sulphuric acid, and then with pure water, dried upon porous tiles, and heated until it begins to acquire a brownish colour; it is then CyS^2Cu^2 without water. 3 parts of dry sulphocyanide of potassium are now fused in an iron vessel, and 2 parts of the above sulphocyanide of copper conveyed by degrees into it, gradually increasing the fire. Sulphuret of carbon is given off, which burns. Towards the end the vessel is heated, so that the bottom is red-hot, as long as a trace of sulphuret of carbon is disengaged, and then about one-eighth of the employed sulphocyanide of potassium of finely-pulverized dry carbonate of potash added*, when a lively disengagement of carbonic acid results. As soon as the

* This addition is not necessary, but it increases the amount of product.

mass flows quietly with a gentle fire it is allowed to cool, water poured over the mass, boiled, filtered, and the mellonide of potassium allowed to crystallize. In this case the sulphocyanide of copper is first decomposed, forming mellon, and this then acts on the sulphocyanide of potassium as above.

c. A mixture of about 40 oz. of slightly-roasted yellow prussiate and 20 oz. of flowers of sulphur is fused, as in the preparation of sulphocyanide of potassium; but instead of stopping when the mass just begins to flow, and is still free from any soluble compound of iron, the fusion is continued in a closed vessel. In this operation the amount of iron first increases, but subsequently again decreases at a higher temperature with evolution of sulphuret of carbon; it finally disappears entirely, and likewise the disengagement of sulphuret of carbon. About one-twentieth in weight of the yellow prussiate employed of carbonate of potash is added to the fluid mass, which is then treated as above. In this instance sulphocyanide of iron is first formed, which subsequently, on its decomposition by heat, affords mellon, which decomposes the sulphocyanide of potassium; and indeed one-third of the entire amount of nitrogen must be obtained as mellonide of potassium*.

The mellonide of potassium so prepared is usually yellowish, and

* A whole third more sulphocyanide of potassium, and this much purer, would be obtained if there were sufficient potassium and sulphur present to form sulphocyanide of potassium with the cyanogen of the protocyanide of iron; with a sufficient quantity of sulphur the fused mass could contain only sulphuret of iron. If, now, on the fusion of the yellow prussiate with sulphur, when the fused mass is observed to contain iron, in which case the solution in water can contain no ferrocyanide of potassium, dry carbonate of potash is added to it, the presence of a considerable quantity of the yellow prussiate is again immediately evident on the removal of the iron; the fused mass, the aqueous solution of which was strongly precipitated by potash, and which precipitated no prussian blue from persalts of iron, contains no more iron after the addition of carbonate of potash, but its solution produces at present a considerable blue precipitate in salts of the peroxide of iron; consequently ferrocyanide of potassium has again been produced from the protocyanide of iron which had remained undecomposed on the addition of carbonate of potash. If, on the contrary, recently fused sulphuret of potassium be added in small portions to the fluid mass, the whole of the iron can be removed, and a larger quantity of sulphocyanide of potassium is obtained, corresponding to the amount of sulphuret of potassium added.

A mixture of 46 parts roasted ferrocyanide of potassium, 17 parts carbonate of potash and 32 sulphur, fuse with the greatest ease. At the commencement of the fusion it is principally the sulphur and carbonate of potash which act on each other, forming with tumescence sulphuret of potassium. If the fusion be continued until the mass flows quietly and clear, and a faint red heat be given towards the end of the operation, the formed hyposulphite of potash is destroyed; and on extracting the mass with alcohol, a perfectly colourless solution is obtained, from which very pure sulphocyanide of potassium crystallizes in perfectly colourless columns. The aqueous solution of the crude mass is free from carbonate of potash, sulphuret of potassium and mellonide of potassium, and contains, besides sulphocyanide of potassium, only sulphate of potash. The iron separates readily from the fluid, as iron pyrites, in fine scales. According to this method one-third more sulphocyanide of potassium is obtained than according to the usual one; it is the simplest and most advantageous mode of preparing the sulphocyanide of potassium.

contains a new compound of potassium containing sulphur. In that case it is separated by solution in warm (not boiling) water, entire precipitation of the solution by acetic acid (by which the above compound is removed), supersaturating the filtered solution with carbonate of potash, and crystallizing; this is repeated if requisite.

Analyses.—It is already evident, from the preparation of the mellonide of potassium, that it can contain neither hydrogen nor oxygen. At the most it would only be possible to admit that the mellonide of potassium, contained in the anhydrous state in the fused mixture, on crystallization from water combines with some, and in such a manner that it cannot be again separated. This view might be advanced on the fact that the mellonide of lead contains water according to Gmelin. Mellonide of potassium and mellonide of silver can however be obtained anhydrous. With respect to the nitrogen and carbon, the author found, like Gmelin, that dry mellonide of lead produces on combustion with oxide of copper N and CO^2, in the proportion by volume of 2 to 3. Dry mellonide of mercury was heated to redness; it did not however decompose into mellon and mercury, and the former again into nitrogen and cyanogen; but it afforded, like hydromellonic acid, at first prussic acid and nitrogen, subsequently nitrogen and cyanogen, in the proportion of 1 to 3.

Mellonide of Silver contains 53·03 per cent. silver, 17·1–18·54 C; the formula $C^6 N^4 Ag$ requires 53·55 Ag, 18·05 C. A small quantity of water was, it is true, obtained, but it only amounted to about one-third of an atom.

Fused *Mellonide of Potassium* contains 28·51 potassium, 25·88–26·37 C; the formula $C^6 N^4 Ka$ requires 29·63 potassium and 27·52 C. Not more than $\frac{1}{9}$ atom of water was obtained.

Mellon.—The preparation of mellon is somewhat difficult. It is obtained by the decomposition of the mellonide of mercury by heat; but unfortunately the combinations of mercury with mellon cannot be procured in a pure state. Both the protonitrate of mercury, as well as corrosive sublimate, afford thick flocculent precipitates with mellonide of potassium. The former on drying becomes gray, and contains intermixed hydromellonic acid; the latter is altered in appearance on the slightest warming, and is decomposed by washing and by contact with the liquid. The purest mellon was obtained by distillation of the mellonide of mercury at a time when of the gas given off three-fourths of its volume were absorbed by caustic potash.

In this state it forms a pale yellow, light powder, which is insoluble in water, alcohol, and in indifferent liquids. Mellon dissolves in caustic potash with evolution of ammonia; the solution contains a salt of potash, which Liebig described formerly, as well as the changes which mellon undergoes by nitric acid, being converted into cyanilic acid. It dissolves entirely in warm hydrate of sulphuric acid, and is precipitated again by water.

Its great affinity for the metals, especially for potassium, is remarkable. The solution of the mellonide of potassium can be boiled with iodine without the slightest decomposition being per-

ceptible. The iodine colours the liquid brown and volatilizes on evaporation, so that at a certain degree of concentration crystallized mellonide of potassium is again obtained. Cyanide of potassium dissolves a large quantity of iodine under similar circumstances; the liquid becomes colourless, and solidifies on cooling to a pasty crystalline mass of iodide of cyanogen, which on heating sublimes in the well-known form of flocculent crystals. Mellon is consequently separated from its combinations by iodine; on the contrary, it liberates the iodine completely from iodide of potassium. A mixture of dry iodide of potassium and mellon fuses, under violent evolution of iodine vapour, yielding mellonide of potassium. When chlorine water is passed through a solution of mellonide of potassium, a white mucilaginous precipitate is formed, which cannot be obtained free from chlorine by washing; it dissolves in ammonia with a yellow colour, under evolution of gas. On fusing mellon in hydrate of potash, cyanate of potash and ammonia are obtained. The formation of this salt is easily explained if we consider that mellon may be regarded as cyanide of nitrogen; on adding to this formula the elements of 3 atoms of water, we obtain ammonia and cyanic acid.

The mellon which remains on heating and igniting the so-called sulphocyanogen, may be employed with the same success in all these experiments; in the action of dry chlorine on a dry mixture of common salt and sulphocyanide of potassium at a gentle heat, there is obtained, by treating the residue with water, a considerable quantity of a pale yellow, laminar, light substance, which after ignition is free from chlorine and sulphur. It behaves like mellon in all its properties.

Taking into consideration the formation and composition of mellon, it does not appear improbable that, under certain circumstances, cyanogen itself can pass into mellon with separation of carbon; the so-called paracyanogen might easily be a mere mixture of carbon with mellon or a carburet of mellon. The observation of Mr. Brown, that paracyanogen parts with all its nitrogen on ignition and leaves behind pure carbon, might readily consist in the mellon being volatilized as nitrogen and cyanogen, while the incombustible carbon remained.

Paracyanide of silver, prepared according to Thaulow from the cyanide of silver, is decomposed at a strong red heat; more than 100 times the volume of cyanogen gas and nitrogen are obtained, although not in the relative proportion which would have been afforded by mellon under these circumstances. The first two tubes contained nitrogen and cyanogen in the proportion of 1 : 8, five others as 1 : 5, 1 : 4, 1 : 8. Mellon would have given nitrogen and cyanogen in the proportion of 1 : 3. Since the paracyanide of silver might contain sesquicyanide of silver, it is conceivable that the proportion of cyanogen may have been increased by the evolution of cyanogen from that compound. At all events this subject deserves a more minute investigation; and the fact that paracyanogen in the silver compound is again converted at a red heat into cyanogen gas, and that a portion of it is decomposed into nitrogen and carbon, is

of considerable interest. Cyanide of silver or paracyanide of silver alone would not have afforded any nitrogen under these circumstances. The gas evolved in the transition of cyanide of silver into paracyanide of silver, and which Thaulow regards as distinct from the ordinary cyanogen gas, exhibited no property in confirmation of this opinion. Potassium burns in it yielding ordinary cyanide of potassium.

The cyanate of silver exhibits, when ignited in a perfectly dry state, the same luminous appearance as cyanide of silver; it evolves a quantity of gas with violence, and if, as is probable, its decomposition proceeds in a similar manner to that of the corresponding sulphur compound, nitrogen and carbonic acid should be obtained in the proportion of 1 : 3, and in the residue mellonide of silver. Some experiments were likewise made to decide this point. Heated alone, the cyanate of silver afforded a mixture of gas, which contained as the mean in the last six tubes for 10 vol. of nitrogen 22 vol. of carbonic acid gas; cyanogen alone would have afforded 20 vol. of carbonic acid to 10 of nitrogen. There had evidently remained a certain amount of nitrogen in the residue; on burning this residue with oxide of copper, there were found in the last 9 tubes of the mixed amount of gas obtained for 100 vol. of nitrogen 137 vol. of carbonic acid. Under these circumstances mellonide of silver would have afforded 150 vol. of carbonic acid to the same (100 vol.) amount of nitrogen.

Hydromellonic Acid.—If a boiling solution of mellonide of ammonium or mellonide of potassium be mixed with nitric or muriatic acid, the liquid remains clear for some moments, but after a short time becomes turbid, and when somewhat concentrated thickens to a brilliant white paste of hydromellonic acid; from a dilute solution it is precipitated by mineral acids in white flakes. The statement of L. Gmelin, that hydromellonic acid is precipitated by acetic acid, relates to the crude impure mellonide of potassium, and in fact to the sulphur compound (perhaps sulphydromellonic acid?) which is mixed with it, and from which it is freed by frequent crystallization.

Hydromellonic acid is in the dry state white, writes like chalk, is very sparingly soluble in cold water, somewhat easier in boiling water; the solution strongly reddens blue litmus-paper; it is insoluble in alcohol, æther, essential and fat oils. It belongs to the stronger acids, since it expels several organic acids from their potash salts. It dissolves on the application of heat with the same ease in acetate of potash as in caustic or carbonate of potash, and this solution solidifies on cooling to a paste of crystals of mellonide of potassium.

Mixed dry with iodide of potassium, it expels hydriodic acid and iodine on the application of heat. Heated alone, it is decomposed at first into nitrogen gas and prussic acid; subsequently it becomes yellow, and yields cyanogen gas, easily known by its purple-red flame. The apparently purest hydromellonic acid leaves behind on ignition in the air a trace of cyanide of potassium or cyanate of potash.

The acid dried at 212° contains no water, for it yields on combustion CO^2 and HO in the proportion of 100 : 23·44.

Although hydromellonic acid does not appear to undergo any change at first by the action of mineral acids, it is nevertheless entirely decomposed when they are allowed to act some time upon it and heat applied. If muriatic or nitric acid be added to a thin paste of recently-precipitated hydromellonic acid, and the mixture kept boiling, the whole is dissolved in the course of from 3 to 4 hours, a clear liquid is obtained, which does not become turbid on cooling, and deposits no hydromellonic acid. If the acid liquid be evaporated to dryness, and be kept at a suitable temperature until the free muriatic acid is removed, a white residue is obtained, which yields sal-ammoniac to water.

Mellonide of Potassium.—A warm saturated solution crystallizes on slowly cooling in minute concentrically-arranged colourless crystals, which are transparent under the microscope, and when it is concentrated it solidifies to a pasty mass of crystals, which contain no water of crystallization. They are insoluble in alcohol, so that an aqueous solution mixed with alcohol becomes instantly turbid, and on standing quiet for some time deposits crystals. Mellonide of potassium crystallizes most beautifully from a hot mixture of equal parts of spirit and water. Mellonide of potassium effloresces in the air, the silky needles become white and lose their lustre; at 238° it loses four-fifths of its water of crystallization; after fusion, or dried at 302°, it is anhydrous. It possesses a very bitter taste, and contains 25·41 per cent., or 5 atoms of water of crystallization.

The last atom of water escapes with slight tumescence from the salt dried between 238° to 302°. The fused salt is thick, yellowish, and solidifies on cooling to an opake crystalline mass, which contracts strongly, producing fissures which are filled with acicular crystals.

Heated beyond its fusing point in closed vessels, mellonide of potassium disengages nitrogen and cyanogen, and there remains cyanide of potassium. Fused, exposed to the air, the mellonide of potassium is oxidized with the greatest ease; two products are principally formed, of which the one is cyanate of potash, the other a potash salt of far more difficult solution. Platinum vessels are violently attacked by fusing mellonide of potassium.

Mellonide of Sodium is best obtained by treating mellonide of barium with carbonate of soda. It crystallizes in white needles, which have a silky lustre, contain water, are insoluble in alcohol and tolerably soluble in water.

Mellonide of Ammonium.—This salt is obtained very pure by the double decomposition of mellonide of barium with carbonate of ammonia. It cannot be distinguished from mellonide of potassium in its external characters, and contains water of crystallization, which escapes at a high temperature. The dry salt, exposed to a higher temperature, parts with ammonia; the residue becomes yellow, and yields similar products to the hydromellonic acid. It is insoluble in alcohol.

Mellonide of Barium.—On adding mellonide of potassium to a solution of chloride of barium, a thick white precipitate is obtained, which dissolves entirely in a large quantity of boiling water. On the cooling of the saturated solution, mellonide of barium separates in transparent short acicular crystals, which contain 6 equiv. of water, 5 of which (20·87 per cent.) escape at 266°.

Mellonide of Strontium is obtained like the mellonide of barium, and differs from this only by its greater solubility in water. A boiling saturated solution solidifies to a paste of fine needles.

Mellonide of Calcium.—By double decomposition of mellonide of potassium with chloride of calcium, a thick white precipitate is obtained, which is still more soluble when warmed than mellonide of strontium, and crystallizes just as easily. The crystals contain 4 equiv. of water, 3 of which (18·05 per cent.) escape at 238°.

Mellonide of Magnesium is still more soluble than the lime salt. A solution of sulphate of magnesia may be mixed with a solution of mellonide of potassium, without immediately producing a precipitate. After standing for some time, the mellonide of magnesium separates in minute white needles. The insolubility of the four preceding salts in saline liquids is remarkable; they are far more soluble in pure water than in water which contains a salt of barytes, strontia, lime or magnesia. This is very evident when a cold saturated solution of one of these salts in pure water, for instance the barytes salt, is added to a solution of chloride of barium, the strontia salt to a solution of chloride of strontium; a very voluminous crystalline precipitate of mellonide of barium, mellonide of strontium, &c., then forms immediately.

Mellonide of Copper is obtained from sulphate of copper and mellonide of potassium in the form of a beautiful parrot-green precipitate, which is but very little soluble in boiling water. 100 parts of the salt, dried at a gentle heat (at 95°), yielded on combustion with oxide of copper 23·94 per cent. water; the salt consequently contains on the whole 5 atoms of water, which correspond to 22·23 per cent. On heating it to 238° it loses four-fifths of its amount of water, becoming black.

The sulphate of the sesquioxide of manganese gives a white gelatinous precipitate with mellonide of potassium, protochloride of copper a bright yellow, salts of cobalt a peach-blossom red, persalts of iron a dark yellow, protosalts of iron a white with a greenish tint, salts of the oxide of chrome a green, tartar-emetic a white. The precipitates are of difficult solution in water.

Mellonide of Silver forms a white gelatinous precipitate, which is anhydrous at 238°.—*Annalen der Chem. und Pharm.*, l. p. 337.

Nature of Fulminic Acid.

Liebig protests against the view recently advanced by Berzelius, an account of which was given in a former Number, p. 512, the absence of hydrogen having been placed beyond doubt by Gay-Lussac and his analyses; besides, the formation of a metallic nitruret in the

presence of a great excess of nitric acid is not probable, leaving wholly out of question the fact that no metallic nitrurets, according to the formula RN. are yet known. It is scarcely possible to explain the easy decomposibility of this or that compound solely from its constitution.—*Annalen der Chem. und Pharm.*, l. p. 429.

On some new Combinations of Platinum.

When, according to M. Peyroné, sulphurous acid is passed through chloride of platinum until sal-ammoniac no longer produces any precipitate, and is then left in a closed bottle, at least three combinations containing no chlorine are formed. The first is almost insoluble in water, the second crystallizes in short colourless stellate groups of needles, the third is extremely soluble, and does not crystallize. All three liberate sulphurous acid on being treated with muriatic acid, and give new chlorides, the first two of which separate in shining lemon- and orange-coloured needles; the third forms a yellow powder.—*Ann. der Chem. und Phys.*, li. p. 28.

On the Decomposition of Metallic Chlorides and Iodides. *By* H. Schlesinger.

The author found that nitric acid decomposes all the chlorides of the alkalies, earths and true metals, with the exception of chloride of silver and perchloride of mercury (chloride of gold and chloride of platinum were not examined), forming nitrates; likewise the iodides, and in this case even the iodides of silver and of mercury; also bromide of sodium. The protochloride of mercury is decomposed, not by the ordinary, but only by fuming nitric acid, into perchloride and nitrate of mercury; the protiodide of mercury is decomposed in a similar manner, but the periodide and nitrate separate as a double salt, which crystallizes in minute colourless laminæ, possessing a strong lustre, and which contain 50 per cent. mercury, 41 iodine, 8 nitric acid, and 1 O, consequently $= 2HgI^2 + HgO$, NO^5. On pouring water over it, it instantly becomes red, and separates into its constituents. Periodide of mercury, which dissolves in nitric acid, and can exist in it for some time unaltered, crystallizes most beautifully on the cooling of the hot nitric solution.

Periodide of mercury is at first rendered brown by fuming nitric acid, with evolution of iodine, and finally passes into a voluminous white body, which is void of smell, has a metallic taste, is insoluble in water, alcohol, nitric and sulphuric acids, and is decomposed by muriatic acid into perchloride of mercury and chloride of iodine, which according to Schlesinger is a superiodide $= Hg^2 I^3$, since it contains 63·7 I and 36·3 Hg. The mother-ley of this body contains nitrate of mercury. Periodide of silver yields with nitric acid nitrate and iodate of silver. All the others appear to be decomposed simply into nitrate and muriatic or hydriodic acid, which latter is soon decomposed into water and iodine.—Buchn. *Repert.*, xxv. p. 74.

Atomic Weight of Bromine.

M. Marignac prepared some bromate of potash from bromine and potash, purified it by repeated crystallization, and converted it by ignition into bromide of potassium; in which operation 100 parts bromate of potash yielded 71·26–71·35 per cent. bromide of potassium (Br = 999·98); further, pure silver was dissolved in nitric acid and precipitated by bromide of potassium; 100 parts silver required 110·28–110·34 bromide of potassium (Br = 999·60); lastly, 100 parts silver gave 174·055, 174·066, 174·072 bromide of silver dried at 392° and fused (Br. = 999·3). The equivalent of bromine therefore is 999·27 or 1000.—Berzelius's *Jahresbericht*, xxiv. p. 73.

Atomic Weight of Iodine.

Marignac found that 100 parts of dissolved silver required 153·65–153·79 iodide of potassium for precipitation (I = 1585·64), and that 100 parts silver gave 217·5–217·54 iodide of silver (I = 1585·54). Millon found that 100 parts iodate of potash, on their conversion into iodide of potassium, gave off 22·46–22·49 oxygen; 100 parts of iodate of silver, on the contrary, 17·03–17·06. Thence results, admitting the equivalent of potassium to be 488·94, for that of iodine 1580·93–1570·73.—Berzelius's *Jahresbericht*, xxiv. p. 75.

Decomposition of Malic Acid by Alkalies.

When, according to M. Rieckher, malic acid or one of its salts is heated with hydrate of potash in excess, a considerable quantity of aqueous vapours escape; the slightly-coloured fused mass hardens on cooling. On examination it was found to contain acetic and oxalic acids, but no formic acid. If bimalate of lime be used for the experiment, exactly the entire amount of oxalic acid remains combined with the lime. 3 atoms of malic acid may in fact be decomposed into 2 atoms of acetic and 2 atoms of oxalic acid.—*Archiv der Pharm.*, xxxix. p. 26.

On the Reduction of the Chloride of Silver.

According to communications from MM. Schmidt, Ricker and Herberger, the decomposition of the chloride of silver by caustic potash, proposed by Professor Gregory as a ready method of obtaining pure silver*, is not complete. The best method, according to M. Ricker, is to mix 1 part chloride of silver with 1 part powdered charcoal and 2 parts nitre, and to convey the mixture in small portions, but quickly, one after the other, into a spacious red-hot crucible, and to maintain it at a red heat for a quarter of an hour, when the regulus may be poured out.—*Jahrb. für Prakt. Pharm.*, viii. p. 293.

* See vol. i., p. 246.

PHARMACOLOGY.

On the Adulteration of Arrowroot with Potato-Starch.
By M. Osswald.

Although much has been written in works on pharmacy respecting the genuineness of arrowroot, the following observations may not be found altogether superfluous.

Some time ago I received a parcel of arrowroot, said to be of the best quality. To ascertain whether it was free from potato-starch, with which it occurs adulterated more frequently than suspected, I adopted the following process:—10 grs. were boiled with an ounce of water, and a few drops of muriatic acid were added to the solution; upon which, after the liquid had been again boiled, a peculiar, somewhat irritating odour was disengaged, resembling that of formic acid. The odour did not disappear, even after some days, but always became stronger on warming the liquid. It is this peculiar smell which indicates the presence of potato-starch, for pure arrowroot, treated in the same manner, does not evolve any peculiar odour. The same result was obtained in an experiment, made for comparison, with 1 part starch and 6 parts arrowroot (7 grs. of which were treated as above), only the odour resembling formic acid was weaker. Other inorganic acids, added to the above mixture, did not give rise to the production of the peculiar odour.

An adulteration with wheat-starch, of which it was free, would have been detected in the following way:—A decoction of 10 grs. in 2 oz. of water would have formed a thick paste and had a pasty smell, while genuine arrowroot forms a more coherent gelatinous compound, and no odour is perceptible on boiling it.

In some works it is stated that, on adding some absolute alcohol to a solution of genuine arrowroot, a separation into two layers takes place; this certainly is the case, but the separation results likewise with adulterated arrowroot, so that this reagent cannot be employed for the purpose of distinguishing between the various kinds of starch. A careful microscopical examination is preferable, as the different kinds of amylon may readily be distinguished by the size and form of the granules.—*Archiv der Pharm.* for Nov. 1844.

Preparation of Iodic Acid.

M. Grosourdy recommends mixing iodine with a solution of chloride of barium, and passing chlorine into it until the whole of the iodine is converted into iodate of barytes, which is then decomposed with sulphuric acid.—*Journ. de Chim. Méd.*, 1843, p. 373.

Vienna Cement for the Teeth.

M. von Wirth first had the idea of stopping hollow teeth with asbestos which had been previously immersed in tooth balsam. This balsam has been successfully imitated by Dr. Ostermeyer of Munich,

but has not been published. It is a solution of West India copal in absolute alcohol, to which some *Ol. Menth. piper.* has been added. This balsam is mixed with finely divided soft asbestos. When the cement is conveyed into the cavity of the tooth, which has been previously well-moistened by means of a brush with a tincture of guaiacum and myrrh, it hardens on the evaporation of the alcohol to a mass, which adheres so firmly that it does not require renewing for several weeks.—Buch. *Repert.*, xxxiii. p. 213.

Some Experiments on the Flowers of Arnica. *By* M. Versmann.

The aqueous infusion of the flowers of *Arnica* is acid, yellowish-brown, and of a bitter irritating taste. It is not altered by tartar-emetic and tincture of galls, is strongly precipitated with acetate of lead and protonitrate of mercury, is rendered opake by a solution of gelatine, affords a dark green precipitate with perchloride of iron, and becomes coloured of a deep green by the addition of pure or carbonate of magnesia. This colour does not arise from pure tannin; gallic acid however presents a similar green colouring with magnesia. When the tannin is precipitated by gelatine from the infusion of *Arnica*, it still affords a dark precipitate with perchloride of iron. Thompson admits the existence of strychnine in the *Arnica*; the author mixed a pound of fresh flowers of *Arnica* with 4 oz. of hydrate of lime, extracted the mixture by displacement with alcohol, distilled off the spirit, evaporated further with the addition of acetic acid, and removed the separated resin. The liquid had neither a strong bitter taste, nor did it produce any precipitate with ammonia.—Buchn. *Repert.*, xxv., p. 47.

On some Substances from the Root of Smilax China.
By H. Reinsch.

When this root is extracted with boiling alcohol, a crystalline substance is dissolved, which the author has named *smilachine*. If the residue be exhausted with spirit of 40 per cent. in order to remove albumen, tannin, mucus and colouring substance, and the undissolved portion be then treated with cold water containing one-tenth alcohol, a yellowish solution is obtained, which, after removing the suspended starch by filtration, is coloured of a dark reddish-brown by tincture of iodine. On evaporation the solution affords a soft extract; the substance which produced the colouring with tincture of iodine is entirely separated by animal charcoal.—*Jahrbuch für Prakt. Pharm.*, viii. p. 291.

Preparation of the Lactate of the Protoxide of Iron.

According to M. Heidlen, it is most advantageous to allow lactate of soda to form in sour milk to which milk-sugar has been added, by the addition of carbonate of soda at 86° to 104°, to coagulate the caseine by heat, after the complete decomposition of the milk-

sugar, to filter, to neutralize the solution accurately with carbonate of soda, to evaporate to the consistence of a syrup, to treat it with from 3 to 4 times the quantity of alcohol of 0·837, to filter again, and to add to the solution obtained a spirituous solution of protochloride of iron, the amount of which may be calculated from the quantity of carbonate of soda employed. The lactate of the protoxide of iron separates in minute crystals, which are collected on a filter and washed twice or three times with spirit.—*Jahrb. für Prakt. Pharm.*, ix. p. 20.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

A Method of ascertaining the Quantity of crystallizable Sugar contained in Beet-root, or other saccharine Substances. By M. Barreswil.

This method is founded upon a peculiar property of sugar, noticed some years ago by M. Trommer, a German chemist. M. Trommer's method consisted in adding to the saccharine solution to be tested a few drops of sulphate of copper, and afterwards of potash, and heating the mixture to nearly a boiling temperature; the uncrystallizable sugar, or molasses, contained in the liquor reduces the salt of copper, and precipitates a red oxide of copper, while the crystallizable sugar contained in the cane does not change the properties of that salt.

M. Barreswil has turned to advantage this reaction, which was well known to chemists, and employed by them as a qualitative test for determining the relative quantities of crystallizable sugar and molasses, when these substances are found either alone, or in combination with other matters, in a solid body like raw sugar, or in a liquid, such as beet-root juice and cane juice. This process is founded on the following facts:—1st, that crystallizable sugar does not reduce the oxide of copper contained in an alkaline liquid; 2nd, that it will reduce this oxide when treated with sulphuric acid, which, on boiling for a few minutes, converts it entirely into uncrystallizable sugar or molasses; 3rd, that the quantity of deutoxide which is reduced is proportionate to the quantity of sugar employed. We will, in a few words, describe M. Barreswil's process.

If it be required to find the quantity of crystallizable sugar contained in a liquid, exclusive of other organic products, an alkaline solution of oxide of copper is to be prepared, by mixing sulphate of copper, neutral tartrate of potash and caustic potash. A liquor of a deep blue colour is thus obtained, which, on being filtered, remains clear and limpid for a long time. This solution is the *test liquor*, the power of which is to be determined by trying how much liquor, made with a certain weight of pure and dry sugar-candy, and raised

to a boiling temperature, will suffice, after the addition of a few drops of sulphuric acid, to decolorize perfectly a given quantity of the testing liquor.

The power of the test liquor having been carefully ascertained, a given quantity is to be poured into a capsule of porcelain or glass, and a suitable quantity of highly-concentrated caustic potash is to be added. The only object of this is to augment the density of the liquid, and to facilitate the ultimate separation of the oxide of copper. As soon as the two liquors come in contact, a yellow precipitate of hydrate of copper is formed, which becomes red, and falls to the bottom of the vessel, on reaching the temperature of the medium in which it was formed. As the operation proceeds, the colour of the liquid becomes less deep, and at the same time the copper is precipitated in the form of protoxide; the operation is complete as soon as the liquid becomes completely colourless. Then, on reckoning upon the graduated vessel the number of divisions which have been employed for arriving at this result, the weight of the sugar contained in the liquor submitted to the experiment may be ascertained.

The essential and delicate part of the operation is to ascertain the exact time when the precipitation of the oxide of copper is complete; this is done by observing the time of decoloration of the liquor, if the saccharine liquor itself be colourless, and also by the cessation of the formation of the opake yellow precipitate which precedes the deposit of the oxide of copper. This latter will only be observed when the substance to be tested is coloured.

An excess of sugar added to the test liquor, after the complete separation of the oxide of copper, gives the well-known brown colour resulting from the reaction of hydrated alkalies upon the uncrystallizable sugar.

If the saccharine liquor to be tested contains crystallizable sugar and molasses, the proportion of this latter substance is ascertained by making a previous experiment with a given portion of the liquid, before submitting it to the action of sulphuric acid; the molasses reduce the copper solution which the crystallizable sugar does not act upon. Another portion of the saccharine liquid is afterwards boiled with the sulphuric acid, so as to convert all the crystallizable sugar into molasses; by means of a second operation, with the liquor thus modified, the total weight of the molasses contained therein is ascertained; and, on deducting therefrom that of the molasses which it contained before (this having been furnished by the first operation), the difference will show the quantity of crystallizable sugar contained in the mixture of water, ordinary sugar and molasses.

M. Barreswil's process is distinguished, as will be seen, by great simplicity; it has been submitted by a committee of the chemical arts to strict trial; it has been ascertained, that when a liquid contains only crystallizable sugar, its proportion may, in a quarter of an hour, be ascertained to the extent of 2 or 3 per cent. It may besides be ascertained, by previous experiment, if the liquor contains the least trace of molasses. When this latter substance is combined with the

sugar, as is the case with cane or beet-root juice kept in the air for some time, or in fraudulent mixtures of brown sugar and granulated molasses, the operation is somewhat less correct.

Having shown the advantages of M. Barreswil's method, we must now speak of its disadvantages. The principal one is, that it is only applicable to pure solutions of sugar, or a mixture of sugar with molasses. In fact, if the substance to be analysed contains tartaric acid, dextrine, sugar of milk, &c., these substances act nearly in the same manner as crystallizable sugar, and might consequently be confounded with it; on the other hand, there exist doubtless some organic matters which have the effect of reducing the alkaline solution of oxide of copper, in the same manner as molasses; so that this process can only be employed with certainty when it shall have been proved by previous experiment that no other organic matters exist in combination with the sugar or molasses, or that they have been separated therefrom by suitable means.

Notwithstanding these disadvantages, M. Barreswil's process is capable of rendering great service to science and manufacture; but there is no doubt that it may be greatly improved by chemists who may make use of it. The committee have accordingly awarded to M. Barreswil a silver medal, and a sum of 1000 francs out of the 3000 francs which were offered to the inventor of a method more perfect and of more general application. It is also decided that the question should be left open for further improvements until the meeting in 1845, and the reward reduced to 2000 francs.—*Bulletin de la Société d'Encouragement*, as inserted in Newton's *London Journal, or Repertory of Patent Inventions* for December.

Detection of Sulphuric Acid in Vinegar.

M. Garnier proposes starch for this purpose. If about 100 grs. of vinegar be boiled with half a grain of starch, and tested from time to time with a solution of iodine, pure vinegar always exhibits the blue colouring; while in a vinegar containing sulphuric acid the colour passes into a wine-red, in consequence of the disaggregation of the starch by the sulphuric acid.—*Journ. de Chem. Méd.*, 1844.

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